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Machinable Dy-containing β-$Ca_3(PO_4)_2$ ceramics

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Abstract

The Dy-containing β-$Ca_3(PO_4)_2$ (abbreviated as β-TCP) ceramics obtained by heating the mixtures of $DyPO_4$ and β-TCP with $DyPO_4$/β-TCP (abbreviated as D/T)=0.10–0.25 in molar ratio sintered at 1300°C for 3 h in air were found to be machinable; they can be drilled and cut easily using conventional inexpensive metallic Fe–Mo–W drills or gravers. The maximum relative density was 97% at 1300°C, over 98% at 1350–1400°C. The bending strength, Vickers' hardness and linear thermal expansion coefficient of the specimens (D/T=0.10–0.25) sintered at 1300°C for 3 h were in the range of 30–50 MPa, 2–3 GPa and 11×10^{-6} °C^{-1}–12×10^{-6} °C^{-1} (20–900°C), respectively.

Keywords: Machinability Dy-containing β-TCP; Xenotime-type $DyPO_4$; Bending strength

1. Introduction

The sintered β-TCP ceramics is used as bioceramics, but not machinable. We first obtained the new machinable dense Dy-containing β-TCP ceramics by heating the mixtures of $DyPO_4$ and β-TCP in air. However, there have been few systematic studies on the machinable Dy-containing β-TCP ceramics, including fabrication method and material properties such as bending strength, Vickers' hardness and thermal expansion coefficient. Several of these are discussed in this paper.

2. Experimental details

β-TCP powder was prepared by heating mixtures of $CaCO_3$ and orthophosphoric acid with $CaCO_3$/P=1.50 in mole ratio at 980°C for 2 h in air. XRD patterns showed β-TCP with smaller amount of apatite ($Ca_{10}(PO_4)_6(OH)_2$, abbreviated as HAp). Xenotime-type $DyPO_4$ powder was prepared by heating monoclinic form $DyPO_4{\cdot}nH_2O$ ($n\leqq2$) at 600°C for 2 h in air [1]. XRD patterns were the same as those of natural xenotime (JCPDS card No.11-254), and no other phases were observed in the powder.

The mixtures of $DyPO_4$ and β-TCP with D/T=0–1.0 in molar ratio were fired at 800°C for 1 h in air, then ball-milled under ethyl alcohol with iron-coated plastic balls at room temperature for 1 day, and finally dried at 110°C for 1 day. The mixed powder was uniaxially dry-pressed at 50 MPa to disks (13 mm in diameter by 5 mm high) or bars (4 mm by 5 mm by 40 mm), before cold isostatic pressing at 100 MPa. Specimens were calcined at 500°C for 1 h and then fired at 1000–1400°C for 3 h.

The 'machinability' of each sintered specimen was tested using conventional metallic Fe–Mo–W drills and gravers. The drilling tests were done using a standard drill press operating at 1700 r.p.m., with a drop of water placed at the drill tip at the beginning of each run. The sintered specimens were mounted on the load cell and tested by manually applying a fixed load of 69 N to the drill, while measuring the times taken to drill holes (3 mm in diameter) of fixed depth (5 mm high). The graving tests were done using metallic gravers for the sintered disks to be cut easier or not.

SEM micrographs were used to evaluate the grain size, using intercept method [2]. Vickers' hardness and linear thermal expansion were measured with a Vickers' hardness meter and with a fused-silica push-rod dilatometer, respectively. Strength testing was conducted in three-point bending on a mechanical testing machine with the bend span of 3.00 cm and a crosshead speed of 0.5 mm min^{-1}.

3. Results and discussion

The phases observed in the specimens fired above 1250°C were α-TCP, β-TCP, xenotime-type $DyPO_4$ and HAp. It is known that pure β-TCP transforms into α-TCP

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above 1180°C in air [3]. This transformation was prohibited by adding $DyPO_4$ to β-TCP. Lattice parameters (a and c axes) of β-TCP fired above 1250°C decreased linearly with increasing mole ratio (D/T) from 0.05 to 0.33, and became constant above $D/T=0.35$ because of the smaller ionic radius of Dy as compared with that of Ca. Dickens et al. [4] reported that β-TCP could be represented by $Ca_{18}[Ca(4)][Ca(5)]_2(PO_4)_{14}$ and impurities might be in the sites of [Ca(4)] and [Ca(5)]. Chemical formula of the β-TCP calculated from solubility limit of $D/T=0.33$ was $Ca_{18}Dy_{1.98}\square(PO_4)_{14}$ (□: vacancy). Two sites of [Ca(4)] and [Ca(5)] were occupied by Dy. Therefore, β-TCP observed in the fired specimens (D/T above 0.05) found to be the Dy-containing β-TCP. One of the reasons that Dy-containing β-TCP ceramics is machinable seems to be due to the formation of the vacancy sites.

The phases of fired specimens above 1250°C were α-TCP and HAp for $D/T=0$–0.01, α-TCP, Dy-containing β-TCP and HAp for $D/T=0.05$, Dy-containing β-TCP and HAp for $D/T=0.10$–0.35, and Dy-containing β-TCP, $DyPO_4$ and HAp for $D/T=0.40$–1.0 in mole ratio. The smaller amount of HAp found in all specimens came from the starting powder of β-TCP as a contaminant.

The bulk densities of the disks fired at 1000°C were almost the same as those of the unheated specimens. However, the disks began to sinter above 1050°C, and their relative density % (100 bulk density/true density) increased with rise in firing temperature. Fig. 1 shows the relation between relative density (%) and D/T in mole ratio. When the specimens ($D/T=0.10$–0.25) were fired at 1300–1400°C for 3 h in air, the relative densities above 95% were achieved. The maximum relative density was 97% at 1300°C, over 98% at 1350–1400°C for $D/T=0.18$. It is known that α-TCP has a loosen structure [5]. Therefore, the relative densities of the specimens ($D/T=0$–0.05) were lower than 85% due to the formation of α-TCP. While the relative density of the specimens (D/T above 0.25) sintered at 1300–1400°C tended to be lower than 95% because of the formation of the mixed structure of Dy-containing β-TCP and $DyPO_4$.

All of the specimens (relative density over 95%) for $D/T=0.10$–0.25 sintered at 1300°C for 3 h could be machined easily without cracking using conventional metallic-working tools. The drilling rate was about 3 mm s^{-1} for the disks ($D/T=0.18$) sintered at 1300°C for 3 h. However, the disks became brittle with rise in sintering temperature above 1350°C due to the grain growth and larger flaw size. After the disks ($D/T=0.18$) sintered at 1300°C for 3 h were engraved or drilled using metallic tool, grain size of the engraved or drilled surface showing transgranular fracture was smaller than 9.8 μm in diameter

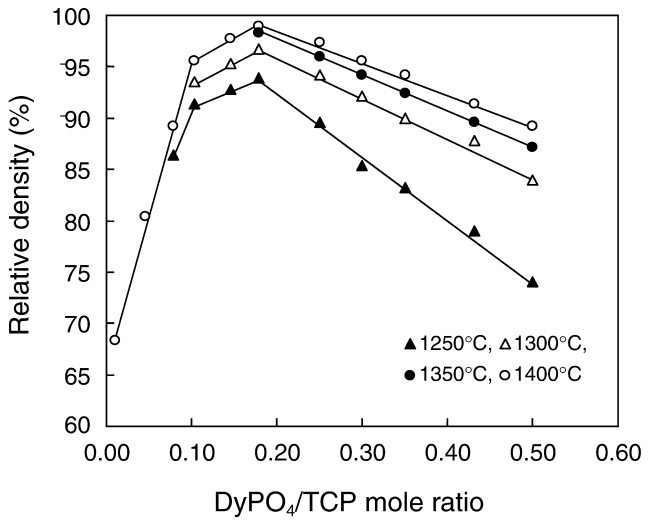

Fig. 1. Relations between relative density (%) and $DyPO_4$/TCP mole ratio. Sintering temperature (3 h): ▲ 1250°C, △ 1300°C, ● 1350°C and ○ 1400°C.

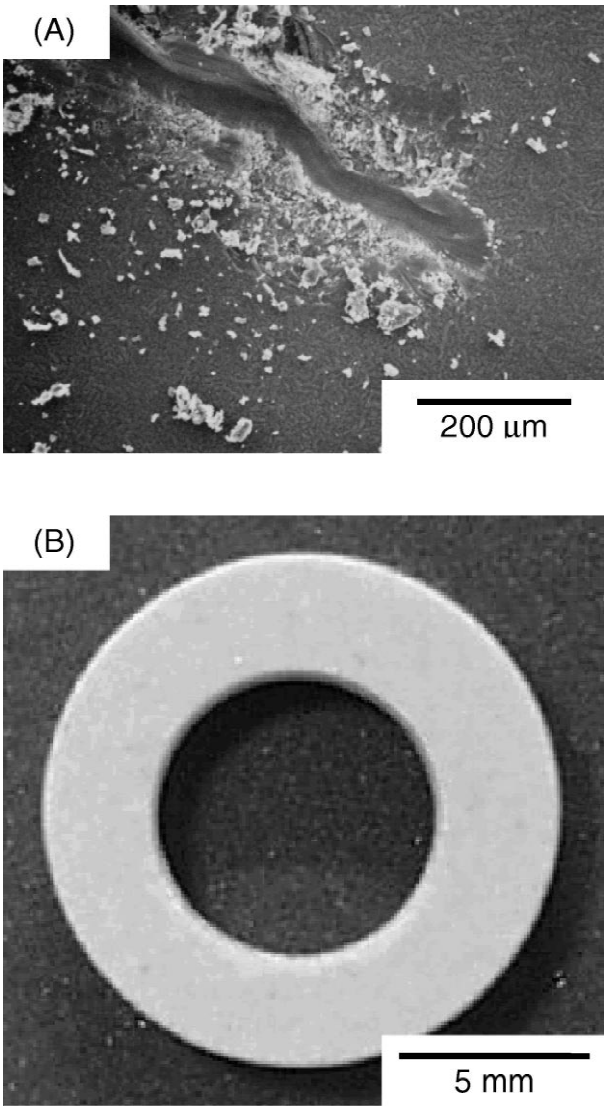

Fig. 2. SEM photographs of (A) engraved surface and (B) drilled hole of the disk ($DyPO_4$/TCP=0.18 in mole ratio) sintered at 1300°C for 3 h in air.

(average grain size before drilling or engraving test). Fig. 2 shows SEM photographs of the engraved surface (Fig. 2(A)) and the drilled hole (Fig. 2(B)) of the disk (D/T= 0.18) sintered at 1300°C for 3 h in air.

Bending strength, Vickers' hardness and linear thermal expansion coefficient of the machinable Dy-containing β-TCP ceramics (D/T=0.10–0.25) sintered at 1300°C for 3 h in air were in the range of 30–50 MPa (room temperature), 2–3 GPa (room temperature) and $11\times10^{-6}\,°C^{-1}$–$12\times10^{-6}\,°C^{-1}$ (20–900°C), respectively. Above 1350°C, increasing sintering temperature tended to decrease the bending strength because of the grain growth and larger flaw size.

4. Summary

In this paper, we made clear the fabrication method and material properties (bending strength, Vickers' hardness and linear thermal expansion coefficient) of the new sintered machinable Dy-containing β-TCP ceramics.

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