INTRODUCTION

For esthetic reasons, considerable attention has recently been given to the clinical use of castable glass-ceramics restorations. The esthetics and strength of glass-ceramics are highly dependent on the ceramming temperature and/or amount of crystal in the glass matrix. However, the volume and size of crystals in the glass matrix are not fully controllable, although they are affected by heating rate, time and temperature. In particular, controlling crystal volume or size within the crystallizing temperature range is difficult and does not always produce consistent results.

In 1989, Kokubo et al. introduced glass-ceramics containing crystalline apatite (Ca₅(PO₄)₃(OH, F)) and magnesium titanate (MgTiO₃) for dental applications. They demonstrated that glass-ceramics precipitating two kinds of crystal have some advantages; excellent esthetics, biocompatibility and excellent mechanical properties. However, the mechanical properties of these glass-ceramics have not been sufficiently investigated for clinical application in dentistry and the crystallizing two kinds of crystal increases the difficulty in elucidating the mechanical properties.

This study investigated the effects of heat treatment after casting (ceramming) on the mechanical properties of castable glass-ceramics containing crystalline apatite and magnesium titanate. The results of investigation may be useful for developing an all ceramic crown using castable glass-ceramics.
STRENGTH OF CASTABLE GLASS-CERAMICS

MATERIALS AND METHODS

Specimen preparation
Castable glass-ceramics* used in this study were composed of SiO₂, CaO, CaF₂, P₂O₅, MgO, TiO₂ and trace compositions. The glass supplied was melted at 1350°C in a furnace**, and cast in a mold by conventional lost wax process using a centrifugal casting machine#. The size of the wax pattern was 3×8×25 mm³.

The cast glassy specimens were reheated to 905°, 925° and 945°C, respectively, at a constant heating rate of 6°C/min, and kept in the furnace for 10 min. After heat treatment for crystallization, the samples were cooled at an average rate of 3°C/min, in the furnace. These reheating temperatures for crystallization were determined by differential thermal analysis (DTA)## at a heating rate of 5°C/min, because the DTA peak for magnesium titanate crystallization is useful in changing the volume of magnesium titanate in glass-ceramics.

Mechanical properties
Test specimens were ground using diamond rasp (#700) measuring 2×7×20 mm³. After grinding, the surface of the specimen was polished flat and smooth by a diamond polishing liquid (average particle size: 0.5 μm). To measure bending strength, 10 specimens at each crystallizing temperature were tested by 3-point bending over a 15 mm span under a cross-head speed 0.5 mm/min. Fracture toughness was measured by Vickers hardness tester*, using the Indentation Micro-fracture method with a load of 0.98-4.9 N. The fracture toughness (KIC) was calculated by the following equation developed by Lawn-Evans-Marshall$	ext{³}$:

\[ K_{IC} = 0.0175 \left( \frac{E}{H} \right)^{1/2} \frac{P}{C^{3/2}} \]

where \( K_{IC} \) is the fracture toughness, \( H \) is the hardness, \( E \) is the elastic modulus, \( P \) is the indentation load, \( C \) is the indentation crack length. Hardness was measured by a Vickers hardness tester.

X-ray diffraction and SEM observation
The X-ray powder diffraction method (XRD)@@ was used to determine the structure and amount of the crystalline phase in the glass matrix. A diffractometer system with a Ni-filter employing CuKα radiation was used. Glass-ceramic surfaces that had been fractured, Vickers indented or etched by hydrofluoric acid were sputtered with gold and observed with a scanning electron microscope (SEM)$.

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* Yata Dental Mfg. Co. Ltd., Osaka, Japan
** Casmic furnace type-M, Yata Dental Mfg. Co. Ltd., Osaka, Japan
# Centrifico, Kerr Manufacturing Co., Romulus, USA
## DT-30, Shimadzu Corp., Kyoto, Japan
@ MVK-E Vickers hardness tester, Akashi Co. Ltd., Yokohama, Japan
@@ ADG-301, Toshiba Co., Tokyo, Japan
$ S-700, Hitachi Co., Tokyo, Japan
RESULTS

X-ray diffraction and SEM observation

The crystal phases of glass-ceramics reheated at various temperatures are shown in Fig. 1. The crystal phase was not observed on the as-cast specimen. The ceramming temperature of 905°C induced apatite crystal of about 30% in the glass matrix. There was no difference in the amount of apatite crystal among ceramming temperatures of 905°C, 925°C and 945°C. However, the volume fraction of the magnesium titanate crystal increased with increases in the ceramming temperature. The volume fraction was approximately 0, 10 and 30% for ceramming temperatures of 905°C, 925°C and 945°C, respectively.

From the micro-structural observations (SEM), the sizes both of apatite and magnesium titanate particles were 0.1–0.2 µm, for the hydrofluoric acid etched specimens. Fractured and Vickers indented surfaces are shown in Figs. 2 and 3. As shown in the fractured surface, heat treated specimens developed deflection and bowing of cracks during destruction. However, deflection and bowing of as-cast specimen was barely observed by SEM. Crack formation in the as-cast specimen with Vickers indentation occurred in a straight-line. Crack formation in the crystallized specimens after ceramming demonstrated zigzag and curved lines.

Bending strength

The bending strengths of glass-ceramics at various ceramming temperatures are summarized in Table 1 and Fig. 4. Bending strength of the as-cast specimen was 90 MPa. The bending strength was increased with increases in the ceramming temperature; 124, 122 and 162 MPa were recorded for the specimens of ceramming temperature of 905°C, 925°C and 945°C, respectively.

Fracture toughness

The relationship between Vickers indentation load and crack length ($C^{1/2}$) are shown in Fig. 5.
5. Since the $C^{2/3} \times 10^{-8}m^{3/2}$ values increased linearly in proportion to the indentation load, fracture toughness of materials could be measured by the Vickers indentation method. Fracture toughness ($K_{IC}$) of as-cast specimens was 0.88 MPa$\cdot$ m$^{1/2}$ (Table 1). However, fracture toughness of specimens reheated at 905°C was twice that of the as-cast specimen, at a value of 1.52 MPa$\cdot$ m$^{1/2}$, as shown in Fig. 6 and Table 1. Fracture toughness was slightly increased with increases in the ceramming temperature. 1.75 and 1.83 MPa$\cdot$ m$^{1/2}$ were calculated for the specimens with a ceramming temperature of 925°C and 945°C, respectively.

**Hardness**

The Vickers hardness ($H_v$) of glass-ceramics at various ceramming temperature are shown in Table 1. As-cast specimens and those treated at 905°C showed the same hardness values. However, hardness values ceramming temperatures above 905°C increased with increases in the ceramming temperature. This result suggests that magnesium titanate possesses a greater hardness than apatite and glassy matrix.
DISCUSSION

The mechanical properties of ceramics with fine particles dispersed through the matrix are known to be affected by the properties of both components, i.e., the physical and mechanical properties of the particles and those of the ceramic matrix\textsuperscript{5-10}. It is difficult to analyze the mechanical properties of the glass-ceramics in which two different kinds of crystals are...
formed. One method of investigating such glass-ceramics is determining the effect of crystalline volume on mechanical properties since the crystalline volumes of two crystals can be controlled by changing the ceramming temperature.

Apatite and magnesium titanate crystals were formed in glass-ceramics at different temperatures. The crystallizing temperatures of apatite and magnesium titanate measured by DTA peaks (Fig. 7) were 760°C and 925°C, respectively. The DTA peak at 735°C showed a segregation into two phases of glass. Thus, when 905°C was employed as the ceramming temperature, the crystalline formed in the glass matrix was almost solely apatite. Therefore, the effect of apatite crystal on the mechanical properties of glass-ceramics was investigated using a specimen cerammed at 905°C. The introduction of apatite particles into the glass matrix did not affect the strength of glass-ceramics even though apatite is a strong particle. This might happen because of apatite ceramics were frail and not very hard. For this reason, the bending strength of glass-ceramics at a ceramming temperature of 905°C
increased only slightly compared to the as-cast specimen. However, the fracture toughness of the specimen cerammed at 905°C increased to two times that of the as-cast specimen. This increase in fracture toughness may be explained by the pinning effect of cracks due to apatite particles7-10,13). Although the apatite crystal is frail, it is strong enough to pin the crack. The other reason may be that the microcrack formed along the surface of apatite crystals. This microcrack was produced by the mismatch of thermal expansion coefficient between apatite and the glass matrix5,11,14).

When glass-ceramics were reheated at 925°C, magnesium titanate crystallized slightly. The crystallization of magnesium titanate formed at this temperature had little or no effect on the fracture strength of glass-ceramics. The size of the magnesium titanate crystalline formed in the glass matrix may be too small for the sufficient crystal growth15, thus affecting fracture strength only slightly. Glass-ceramics produced at ceramming temperature of 945°C showed both higher bending strength and higher fracture toughness. As shown in Figs. 2 and 3, increases of the strength and fracture toughness occurred because of the crack deflection effect5,11). Magnesium titanate was abundantly produced as crystalline particles, and this maybe have induced higher mechanical properties in glass-ceramics cerammed at 945°C. The results of the hardness test support the above speculation, the magnesium titanate crystal was harder than apatite crystal or glassy matrix (Table 1). The hard particle is known to be more effective in crack deflection, bowing and pinning of the ceramics15). In this experiment as well, the strength of glass-ceramics was increased more by the crystallization of magnesium titanate than by that of apatite.

Sumii reported that a bending strength above 100 MPa is required for castable glass-ceramics16). Commercial body dental porcelains have a bending strength of about 100—130 MPa17). The glass-ceramics used in this study showed a higher strength than commercial porcelains. Therefore, these glass-ceramics seem to have a potential value for a clinical application at least with respect to the mechanical properties.

CONCLUSION

The respective contributions of crystalline apatite and magnesium titanate to the fracture strength of castable glass-ceramics were investigated by changing the ceramming temperature.

Both bending strength and fracture toughness of glass-ceramics increased after crystallization compared to those of as-cast specimens. Measuring the fracture strength suggested that the crystallization of magnesium titanate is more effective in improving the strength than that of apatite. This increase in fracture strength was considered due to the extreme hardness of magnesium titanate crystal compared with that of apatite crystal. The glass-ceramics containing crystalline apatite and magnesium titanate after crystallized at 945°C showed higher strength and fracture toughness than commercial body porcelains.

REFERENCES

STRENGTH OF CASTABLE GLASS-CERAMICS

197-202. (in Japanese)


2種の結晶を含有するキャスタブルガラス
セラミックスの機械的強さに及ぼす結晶化の影響
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アパタイトとチタン酸マグネシウムの2種の結晶が析
出するキャスタブルガラスセラミックスの機械的性質に
及ぼす結晶化（セラミング）の影響を検討するため，結
晶化処理温度を変化させ，曲げ強さ，破壊靭性および硬
さなどを調べた．その結果，結晶化処理したガラスセラ
ミックスの曲げ強さは結晶相の増加について高くなるこ
とがわかった．ガラスセラミックス中に析出するチタン
酸マグネシウムは同量のアパタイトの析出に比較し，強
さに対して効果的であることが示唆された．破壊靭性は
アパタイト結晶だけを析出させた試験片で，アズキャス
トの場合に比較して，2倍の値が得られた．このことは
硬さの低いアパタイト粒子でもクラックのピニング止め効果
を持つものと考えられた．本材料は市販のポディー用陶
材より高い機械的性質が得られたことから，審美補綴材
料として使用できる可能性が示唆された．

O-メタクリロイル-N-アシルチロシンの合成と無処理人歯象牙質に対する接着性
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岡山大学歯学部歯科理工学講座

接着性モノマーの分子構造と接着性との相関を調べる
ことを目的として，様々な長さのアシル鎖を持つO-メタ
クリロイル-N-アシルチロシン（MAATY）を合成，そ
れらを含むボンディング剤を調製し，その無処理人歯象
牙質に対する接着強さについて検討した．その結果は，
チロシン骨格のカルボキシル基の自由度の増大が歯質と
の相互作用にとって好ましく強固な接着の要因であると
考えられた．又，立体障害，礫水性といったカルボキシ
ル基近傍の構造，モノマー分子の礫水性－親水性のバラ
ンス，共重合系の重合収縮が重要であることが示唆され
た．特に，カルボキシル基の架橋基の立体障害がO-メタ
クリロイル-N-オクタノイルチロシンの場合には極めて
重要であった．最大接着強さはO-メタクリロイル-N-
ヘキサノイルチロシン（15 mol %）-HEMA（85 mol %）
から成るボンディング剤で得られた．その接着強さ（4.75
MPa）はフェニルアラニンを骨格に持つメタクリレート
のうちで最大であった．

リン酸で処理した象牙質への接着における銅イオン含有プライマーの効果
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象牙質界面での重合を促進することが可能な銅イオン
を含むプライマーについて検討した．牛歯象牙質表面を
10％リン酸水溶液で前処理した後，0.03％の銅塩を含
む35％2-ヒドロキシエチルメタクリレート（HEMA）
水溶液からなるプライマーを塗布し，4-META/MMA-
TBBQレジンで接着した．このプライマーを用いること
により，プライマーを用いないときの接着強さ3.8
MPa，あるいは銅塩を含まない35％HEMAプライマー