(Short Communication)

Hydrated Behaviors and Mechanical Properties of Silicate-Containing Dental Glass Ceramics

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(Received September 22, 1999; Accepted November 30, 1999)

ABSTRACT

Several silicate-containing dental ceramic glasses with the composition xMO_y - zAl_2O_3 - SiO_2 (M = Na, K, Ca, Ba) were studied. The cations Ca⁺², Ba⁺², and Na⁺ were used to replace K⁺ in the glass structures. Under a hydrolytic resistance test according to ISO standards, some of these ceramic glasses had weight loss of less than 0.05%, which indicates a 30-year life span for dental applications in the oral environment. Hydrated ceramic glasses were found to have better mechanical properties than glasses without hydration, with approximately 20% greater flexural strength. Possible strengthening mechanisms for the hydrated ceramic glasses are explained. Furthermore, the powder preparation, microstructure, and hydration behaviors of these dental ceramics are discussed.

Key Words: mechanical properties, microsturcture, hydration, dental materials, glass ceramics, alloy design

I. Introduction

Due to their excellent esthetic appearance and chemical durability in the oral environment, glass ceramics have been used in dental applications. Several researchers have studied the chemical durability of glass ceramics under different conditions (Wu, 1980; Wu et al., 1986; Kao, 1986; Moriya and Norgami, 1980; Oliveira et al., 1995). Glass modifiers such as Na^+ , K^+ , and Ca^{+2} have been minimized to prevent large weight loss under hydration. Recently, a commercialized dental ceramic has been developed (DUCERA, 1993). Besides for its good chemical durability, this dental glass can be fully densified at low temperatures (~600°C). In the oral environment, its mechanical properties are important because of the formation of a hydrated layer. This commercial dental glass has the same composition as the glass ceramic in the (K, Na)₂O-Al₂O₃-SiO₂ system we studied previously (Sheu et al., 1994).

In the system (K, Na)₂O-Al₂O₃-SiO₂, glass ceramics have different thermal expansion coefficients 9–15 ppm/°C at 25°–700°C under variation of the Na and leucite (K₂O-Al₂O₃-4Si₂O) contents (Sheu *et al.*, 1994). With such a wide range of the thermal expansion coefficient, these glass ceramics can match different thermal properties of materials such as ceramics, metals, or polymers in dental applications. A previously published (K, Na)₂O- Al₂O₃-SiO₂ phase diagram (Levin *et al.*, 1964) indicates that the system (K, Na)₂O-Al₂O₃-SiO₂ has lower liquidus temperatures between (K, Na)₂O-Al₂O₃-4SiO₂ and (K, Na)₂O-Al₂O₃-6SiO₂. Therefore, dental glasses in the system (K, Na)₂O-Al₂O₃-SiO₂ are expected to have sintering temperatures lower than those in the system K₂O-Al₂O₃-SiO₂. To further improve the hydration and sintering behaviors, dental glass ceramic with a composition of *x*(K, M_{1/z'})₂O-yAl₂O₃-zSiO₂ (M = K, Ca, Ba; *z*' = charge of cation M^{+z'}; *x* = *y*) was chosen for this study. This is because dental glass has a very small number of non-bridging oxygens in the glass structure when (K, M_{1/z'})₂O/Al₂O₃ = 1 (*x* = *y*), therefore cations, such as Na⁺ and K⁺, are not easily leached out in the oral environment.

II. Experimental Procedures

The raw materials were Al(NO₃)₃-9H₂O, 99.9% pure TEOS, 99.9% pure K₂CO₃, 99.9% pure Na₂CO₃, 99.9% pure CaCO₃, and 99.9% pure BaCO₃. Each carbonate was dissolved in HNO₃ plus H₂O to form a liquid solution. Al(NO₃)₃-9H₂O was dissolved in distilled water. According to the composition along $x(K, M_{1/z'})_2O$ -yAl₂O₃-zSiO₂ (M = K, Ca, Ba; z' = charge of cation M^{+z'}), two different aqueous solutions were initially mixed inside two separate beakers. One was acid, TEOS and Al(NO₃)₃-9H₂O; the other was base, HNO₃ plus carbonate solutions. Subse-

quently, NH₄OH, the acid, and the base solutions were mixed together. The mixed solution was then continuously stirred until a gel-like solution formed. The gel-like solution was dried in an oven or illuminated with an infrared light to remove the liquid. The dried powders were calcined at $650-750^{\circ}$ C in air for 1 h to form oxides. The calcined powders were die-pressed at room temperature and then were sintered at $750-1350^{\circ}$ C for 1 h.

The hydration behaviors of the tested specimens were studied a Soxleth extraction device for 16 h while following ISO standards. Before hydration, the specimens were polished using Al_2O_3 grinding medium down to 0.05 μ m. The aqueous solution for hydration was 4% acetic solution, and the temperature was set at approximately 80°C.

A three-point bending fixture with a 12-mm span was used to measure the flexural strength of the tested specimens. The strain rate was controlled at 0.001/s. The phase existence was determined using the X-ray diffraction method. The microstructure was observed using a scanning electron microscope (SEM).

III. Results and Discussion

1. Powder Preparation and Phase in the Sintered Specimen

Figure 1 shows the TGA (thermogravimetry analysis) and DTA (differential thermal analysis) curves of the co-precipitated powders. The heating rate for the TGA and DTA curves was 10°C/min. During heating, in the TGA curve, the co-precipitated powders had significant weight loss at T = 220°C. When T > 740°C, these powders did not show any significant weight loss. The corresponding DTA curve also shows an exothermic chemical reaction at T = 220°C. When T > 220°C, there was no chemical reaction. The DTA curve indicates that the transformation between hydroxide and oxide was probably completed after the exothermic chemical reaction at T = 200°C.



Fig. 1. TGA and DTA curves of the co-precipitated powder during heating.

220°C. Therefore, the calcination temperature was at 740°C or lower to obtain fine powders.

Most of the sintered glass ceramics contained leucite $(K_2O-Al_2O_3-4SiO_2)$. The leucite phase was mainly in the crystal structure of low leucite. However, if K⁺ was partially replaced with Ba⁺², some high leucite was retained at room temperature. The corresponding X-ray diffraction is shown in Fig. 2. This probably occurred because large cations, such as Cs^+ or Ba^{+2} , help to stabilize high leucite at low temperatures. The stabilization effects of these large cations for high leucite are still under investigation in our laboratory. In the (K, Na)₂O-Al₂O₃-SiO₂ system, the sintered glass ceramics were found to contain low leucite but not high leucite. The low leucite phase was precipitated in the glass matrix with a size $< 1 \mu m$, as shown in Fig. 3. The amount of leucite in the glass ceramic depends on the composition and the fabrication processes. The phase region of leucite can be seen from the (K, Na)₂O-Al₂O₃-SiO₂ phase diagram (Levin et al., 1964).



Fig. 2. X-ray diffraction patterns of a sintered specimen in the (K₂, Ba)O-Al₂O₃-SiO₂ system.



Fig. 3. Typical fractural surface of a glass ceramic. Leucite precipitates are uniformly distributed in the glass matrix. The scale bar is 4 μ m.

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Table 1.	Weight Loss	es for Differei	nt Glass Cerar	nics after Hydration

Sample	Composition	Weight Loss (%)
A1	Na1.8Ba0.1Al2Si4O12	0.11
A2	K _{0.9} Na _{0.9} Ca _{0.1} Al ₂ Si ₄ O ₁₂	0.68
A3	$K_{0.9}Na_{0.9}Ba_{0.1}Al_2Si_4O_{12}$	0.20
A4	K _{1.0} Na _{1.0} Al ₂ Si ₅ O ₁₄	0.13
A5	K _{0.9} Na _{0.9} Ca _{0.1} Al ₂ Si ₅ O ₁₄	0.11
A6	Na _{2.0} Al ₂ Si ₆ O ₁₆	0.04
A7	Na _{1.8} Ca _{0.1} Al ₂ Si ₆ O ₁₆	0.06
A8	Na _{1.8} Ba _{0.1} Al ₂ Si ₆ O ₁₆	0.11
A9	K _{0.9} Na _{0.9} Ba _{0.1} Al ₂ Si ₆ O ₁₆	0.11
B1	$K_{2,0}Al_2Si_4O_{12}$	0.000
B2	$K_{1.6}Na_{0.4}Al_2Si_4O_{12}$	0.009
B3	$K_{1,2}Na_{0,8}Al_2Si_4O_{12}$	0.003
B4	$K_{0.8}Na_{1.2}Al_2Si_4O_{12}$	0.004
B5	$K_{0.4}Na_{1.6}Al_2Si_4O_{12}$	0.003
B6	$Na_{2.0}Al_2Si_4O_{12}$	0.018

2. Hydration Behavior

Table 1 lists the weight losses of the glass ceramics after hydration. The tested specimens are divided into two groups, A and B. Group A represents cation Na⁺ or K⁺ replaced by cation Ba⁺² or Ca⁺². Samples A4 and A6 serve as references. Group B represents cation K⁺ partially or completely replaced by Na⁺. From Table 1, the glass ceramics in group B have better hydration resistance behaviors than do those in group A. This indicates that the divalent cations Ca⁺² and Ba⁺² in the glass structures are not good for hydration resistance if compared with the univalent cations K⁺ and Na⁺. The inferior hydration resistance of glasses containing Ca⁺² and Ba⁺² is probably related to the increased amount of non-bridging oxygen.

Figure 4 shows infrared spectra for the hydrated and non-hydrated specimens. The hydrated specimen shows significant absorption at a wavelength number \sim 3500/cm due to the presence of OH- bonds. The non-hydrated specimen shows little absorption at the same wavelength. This is probably due to the smaller amount of H₂O ab-



Fig. 4. Infrared spectra of hydrated and non-hydrated specimens.

sorbed during sample preparation.

Figure 5 shows an SEM micrograph with the K⁺ concentration profile along the thickness direction for hydrated sample B5. The hydrated layer is located in the dark area with a low concentration profile of K⁺. In this type of (K, Na)₂O-*x*Al₂O₃-*y*SiO₂ glass ceramic, K⁺ and Na⁺ are leached out from the hydrated layer. With a smaller amount of K⁺ in the hydrated layer, its secondary electron image is much darker than the image of the non-hydrated area. The hydrated layer of this particular sample shown in Fig. 5 was approximately 1 μ m in thickness. It is worth mentioning that the specimens shown in Fig. 5 were carefully prepared so as to let the hydrated layers come into contact with each other in the center areas to prevent the edge effect from occurring in the SEM micro-



Fig. 5. An SEM micrograph with K^+ concentration profile along the thickness direction of hydrated specimen B5. The straight line A is for the position of the line scan; the curved line B is for the K^+ concentration profile. The arrow indicates the free surfaces of two hydrated speciments. The scale bar is 4 μ m.

 Table 2. Flexural Strength of Non-hydrated and Hydrated Glass Ceramics;

 specimen Indices Refer to Table 1

Sample	Before Hydration (MPa)	After Hydration (MPa)
A1	92.2 ± 6.3	103.7 ± 21.6
A2	76.5 ± 32.6	43.8 ± 8.1
A3	103.3 ± 47.6	113.3 ± 27.7
A4	113.8 ± 19.9	128.8 ± 3.7
A5	140.9 ± 94.7	215.3 ± 101.2
A6	88.0 ± 18.5	111.5 ± 19.9
A7	67.5 ± 5.7	105.3 ± 21.7
A8	93.9 ± 31.3	103.0 ± 12.0
A9	140.5 ± 13.7	154.5 ± 21.9
B1	92.9 ± 39.0	93.1 ± 31.9
B2	118.8 ± 21.0	161.2 ± 58.8
B3	98.3 ± 9.4	139.0 ± 11.0
B4	89.0 ± 19.8	129.5 ± 21.6
B5	84.1 ± 2.3	93.6 ± 7.1
B6	83.4 ± 21.8	80.3 ± 11.0



(a)



(b)

Fig. 6. SEM fractographs of (a) sample A2 and (b) sample A5. The scale bars are 40 μ m.

graph.

3. Mechanical Properties of Hydrated Glass Ceramics

The mechanical properties of non-hydrated and hydrated glass ceramics are listed in Table 2. In these hydrated and non-hydrated specimens, their composition seems to not be a determining factor for the flexural strength. Except for samples A2 and B6, the hydrated glass ceramics had better flexural strength than the nonhydrated one. Two representative microstructures shown in Fig. 6 indicate that the hydrated A2 specimen had larger pores than the hydrated A5 specimen. The larger pore size was approximately 30 μ m in the hydrated A2 specimen and 4 μ m in the hydrated A5 specimen. Due to the presence of large pores, the hydrated A2 specimen had inferior flexural strength. Therefore, it is believed that the strengthening mechanism of the hydrated layer is sometimes overshadowed by the pore size effect when the hydrated layer is not thick enough.

IV. Conclusions

In this study, silicate-containing dental glass ceramics in which cation K^+ was replaced with cations Ca^{+2} , Ba^{+2} , and Na^+ were studied to determine their hydrated behaviors and mechanical properties. Glass ceramics with univalent cations Na^+ and K^+ had better hydration resistant behaviors than did those with divalent cations Ca^{+2} and Ba^{+2} . Hydrated specimens had better mechanical properties than non-hydrated ones and had approximately 20% more flexural strength. However, due to their large pores, some of the hydrated specimens had inferior mechanical properties.

Acknowledgment

The authors would like to thank the National Science Council of the Republic of China for financial support of this research.

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氧化矽基牙齒玻璃陶瓷的水解性和機械性質

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摘要

本研究是以成份為xMO_y-zAl₂O₃-SiO₂(M = Na, K, Ca, Ba)之矽酸氧化物的陶瓷牙齒玻璃為探討對象。其中金屬陽離子 Ca⁺², Ba⁺², Na⁺ 是被用來取代在玻璃結構中的K⁺。依据ISO 抗水解試驗的標準,我們發現大部份的矽酸氧化物的玻璃陶 瓷,在水解測試的實驗中其重量損失是在0.05%以下。在此低重量損失的特性下,這些玻璃陶瓷被認為在口腔環境下可以 維持將近有30年的壽命。水解的玻璃陶瓷比非水解的樣品之機械性能優良,在彎曲強度方面大約高出20%。除此之外,水解玻璃陶瓷的增韌機構將加以解釋。而且陶瓷牙齒玻璃的粉末製備、微觀組織、以及水解特性則分別詳加討論。