Developmental Study of Functional Glass Ceramics

Part 2 DTA-TG Analysis of Powder Mixtures Applied for Dental Purpose

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ABSTRACT

A preliminary application of new ceramics was carried out using powder mixtures. First, three types of powders (caolinite, solidum silicate (liquid) and sodium silicate (solid)) were mixed to an apatite-based glass ceramic, 20 wt%CaO/10 wt% P_2O_5/10 wt%MgO/10 wt%Al_2O_3/50 wt%SiO_2, and conventional porcelain ceramics were used as control samples. Secondly, using CaO and P_2O_5 powders as main chemical compositions in the first three powder mixtures, their powders were mixed with 5, 10, 15, 20, 25, 30 and 35 wt% of CaO in the binary mixtures. Their thermal properties of powder mixtures were examined by differential thermal analysis (DTA) and thermogravimetry (TG) during a heat to 1100°C. The effect of powder compositions used in this study (caolinite and sodium silicate) on thermal behaviours were clarified. That is, the oxide compositions of Al_2O_3 and SiO_2 in the caolinite mineral raised to higher crystallization temperature, and the oxides, Na_2O and SiO_2, in the sodium silicate lowered the melting temperature. Base on these DTA and TG results, binary CaO/P_2O_5 powder mixtures had the temperature range of crystal formation before higher decomposition temperature. These thermoanalytical results of ceramming treatment of binary new ceramics can be applied to newly-designed glass ceramics.

INTRODUCTION

The chemical composition and surface treatment were very important factors to evaluate mechanical strength[1] and biologic responses[2]. Dental feldspathic and aluminous porcelain ceramics were used for their esthetic performance[3, 4], and all-ceramic restorations had more superior mechanical strengths than those of feldspathic porcelains[4]. It is known that all-ceramic restorations were used less than porcelain-fused-to metal crowns[4, 5]. Industrial ceramics and processing techniques were applied to develop new glass ceramics, based on clinical studies over the past 30 years[6]. Fractography study clarified the crack origin and the crack path from the clinically failed restorations, showing that the crack came from the internal surface[7]. Newly-designed apatite-based glass ceramics were developed preliminarily[8-13], based on the developmental study of crystallized treatment of amorphous glass matrix. That is, fracture-surface analysis examined that aluminous and glass ceramic central porcelains and dental ceramics had the cracks on the fracture surface[14-20], and the crack initiated and propagated from the internal surface at the level of in vivo stress at failure. From these results, it was important to obtain the ceramic composites including the strengthened crystals within the amorphous glass matrix. Thus, thermal analysis has been carried out to clarify thermal properties of glass ceramics, to produce the ceramic composites by the appropriate thermal treatment to crystallize the amorphous glass matrix, so-called ceramming treatment. In this fundamental study, thermal behaviours of

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newly-designed binary glass ceramics including three types of minerals in apatite-based glass ceramic were measured by differential thermal analysis and thermogravimetry, and their compositions were examined to develop the functional binary CaO/P_2O_5 glass ceramics.

MATERIALS AND METHODS

1. Binary powder mixtures of glass ceramics

The materials used were three types of powders, caolinite, liquid sodium silicate and solid sodium silicate. The caolinite ($Al_2O_3 \cdot 2.183SiO_2 \cdot 2.160H_2O$), which was obtained by Faculty of Science, Hiroshima University (Higashi-Hiroshima City, Japan), was supplied for dental purpose. The liquid and solid sodium silicate were $Na_2O \cdot 2SiO_2$ (Wako Junyaku Kougyou, Osaka, Japan). These powders were mixed to a newly - designed apatite - based 20 wt%CaO/10 wt% P_2O_5/10 wt% MgO/10 wt% Al_2O_3/50 wt% SiO_2 glass ceramic (noted as AC)[8-13]. The mixing ratios of caolinite/AC were 100/0 (A0), 70/30(A1), 50/50(A2), and 1/2(A3). In case of liquid sodium silicate/AC, the mixing ratios of liquid sodium silicate/AC were 100/0(B0), 70/30(B1), 50/50(B2), and 1/2(B3). These mixed powders were heated to 900, or 1200° C. Also, in case of solid sodium silicate/AC, the mixing ratios of solid sodium silicate/AC were 100/0(C0), 70/30(C1), 50/50(C2), and 1/2(C3). Commercial porcelain ceramics (Cera 8/enamel (CE) and Cera 8/dentine (CD); Tohwa Giken Co, Osaka, Japan) were used as control samples. Secondly, binary CaO/ P_2O_5 powder mixtures were mixed with 5, 10, 15, 20, 25, 30 and 35 wt% of CaO to binary mixtures. The CaO and P_2O_5 powders were supplied by Wako Junyaku Kougyou. The powder samples were mechanically mixed, and subjected to the thermal analyses.

2. Thermal analyses

DTA and TG analyses were carried out using DT 30 and also DT 50 (Shimadzu Co, Kyoto, Japan). The measuring condition was as follows. At a heating rate of 10° C/min, the samples (weight = 30 mg) were heated from room temperature (22° C) to 1000° C under DTA or TG analysis. The reference weight of alpha alumina was 30 mg. The nitrogen gas flow was 3 ml/min. On DTA curves, endothermic (decomposition or melting) and exthothermic (crystallization) peak temperatures were measured. On TG curves, the weight loss associated with thermal decomposition was detected.

RESULTS

Figure 1 shows schematic figures of endothermic (decomposition; TE1, TE2, and TE3) and exothermic (crystallization; TC) peak temperatures on DTA curve when heated to 1100° C. Thermal properties of the samples (caolinite/apatite-based glass ceramic) are indicated in

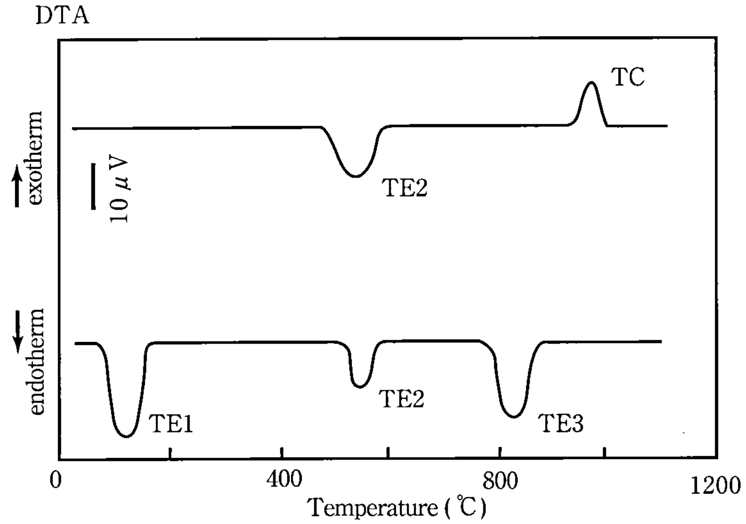

Figure 1 Schematic figures of endothermic (decomposition; TE1, TE2, and TE3) and exothermic (crystallization; TC) peak temperatures on DTA curve when heated to 1100° C.

Table 1, showing their endothermic reaction peak (TE2) and crystal formation (TC) during heating to 1100°C. The endothermic peaks were detected around 520°C, and the crystal formed around 995°C. As reported early[9,10], the crystal at about 1000°C was leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$) at the leucite zone of the porcelain ceramics, but the crystal was mullite ($3Al_2O_3 \cdot 2SiO_2$) after the dehydration of H_2O in the Al_2O_3/SiO_2 ceramic zone of apatite-based glass ceramic powders used as one of binary mixtures. Table 2 indicates three endothermic temperatures (TE1, TE2, TE3) of the samples (liquid sodium silicate/apatite-based glass ceramic) detected on DTA curves, showing that the schematic curves are in Fig 1. The powders which were mixed or used after heating 900 or 1200°C showed almost the same DTA behaviours which had two or three endothermic peak temperatures. The sodium silicate (liquid) decomposed at lower temperatures of 120°C. After heating 900 or 1200°C, the thermal decomposition of the sodium silicate-added apatite based glass ceramic appearred at higher temperatures (around 1000°C), as compared with liquid sodium silicate (B0). In Table 3, the endothermic peak temperatures (TE1, TE2, TE3) are indicated for solid sodium silicate/apatite-based glass ceramic powder mixtures. At higher temperatures, their DTA behaviours were different among the samples, showing that C2 sample decomposed at more than 960°C. Table 4 indicates the endothermic temperatures (TE1,TE3) of commercial porcelain ceramics. At TE1 temperature, the water dehydrated from the powders, and also the compositions at the $K_2O/Al_2O_3/SiO_2$ ceramic zone were decomposed at TE3 temperature after the formation of mullite.

Table 1 Thermal properties of the samples (caolinite/apatite-based glass ceramic) which show endothermic reaction peak and crystallization temperatures during heating to 1100°C. See text for key.

Code	Peak temperatures (°C)	
	TE2	TC
A0	527.1 (14.1)	995.5 (0.7)
A1	520.7 (5.7)	995.0 (1.2)
A2	525.0 (3.5)	999.0 (2.5)
A3	521.0 (0.0)	996.5 (0.0)

Figure 2 shows DTA and TG curves of glass ceramics (CaO/P_2O_5 = 5, 10, 15, and 20 wt%), and the weight losses were found for each case tested and the exothermic peaks were detected between TE1 and TE3. Figures 3 shows DTA and TG curves of binary glass ceramics (CaO/P_2O_5 = 25, 30, and 35 wt%), and the weight losses were not found on TG curves. Before the TE3 temperatures, there appeared an exothermic temperature range related to crystallization.

DISCUSSION

DTA and TG analyses has clarified thermal behaviours of thermal-induced decomposition and crystallizaion of the dental materials[10,21,22]. The thermal changes in glass ceramics (ceramic composites) which were composed of powder minerals occurred within the amorphous glass matrix (Tables 1 to 4), and new crystals appearred associated with thermal decomposition (Figs 2, 3). This study clarified that the thermal decomposition and crystallization determined the conditions of synthesis

Table 2 Thermal properties of the samples (liquid sodium silicate/apatite-based glass ceramic) which show endothermic reaction peak temperatures during heating to 1100°C. The powders were mixed mechanically (mix), or used after heating to 900 or 1200°C. See text for key.

Code		Peak temperatures (°C)		
		TE1	TE2	TE3
B0		123.0 (0.0)	561.0 (0.0)	856.0 (0.0)
B1	Mix	120.0 (3.7)	576.7 (2.1)	1025.7 (6.6)
	900°C	-	574.3 (9.1)	1020.0 (3.5)
	1200°C	-	572.0 (0.0)	1020.0 (0.0)
B2	Mix	120.0 (4.2)	590.7 (2.9)	912.7 (7.9)
	900°C	-	556.7 (7.4)	981.0 (0.7)
B3	Mix	181.7 (14.6)	579.3 (6.4)	966.7 (28.4)

Table 3 Thermal properties of the samples (solid sodium silicate/apatite-based glass ceramic) which show endothermic reaction peak temperatures during heating to 1100°C. The powders were mixed mechanically. See text for key.

Code	Peak temperatures (°C)		
	TE1	TE2	TE3
C0	114.5 (0.7)	580.0 (0.0)	735.0 (4.9)
C1	63.0 (1.4)	570.0 (12.2)	756.7 (12.4)
C2	110.3 (4.6)	571.7 (2.1)	961.7 (12.4)
C3	60.0 (0.0)	570.0 (14.1)	737.5 (10.6)

Table 4 Thermal properties of the control samples which show endothermic reaction peak temperatures during heating to 1100°C. The powders were mixed mechanically. See text for key.

Code	Peak temperatures (°C)	
	TE1	TE3
CE	90.5 (0.7)	985.0 (7.1)
CD	89.7 (0.4)	982.5 (3.5)

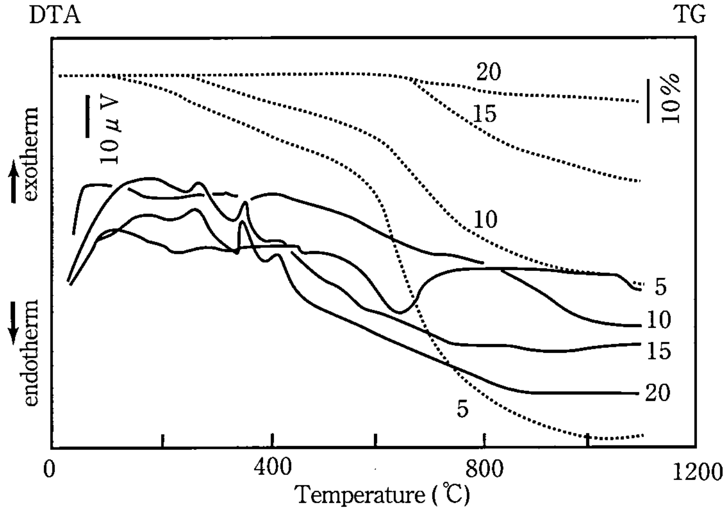

Figure 2 DTA and TG curves of glass ceramics (CaO/P_2O_5 = 5 ,10, 15, and 20 wt%) when heated to 1100°C.

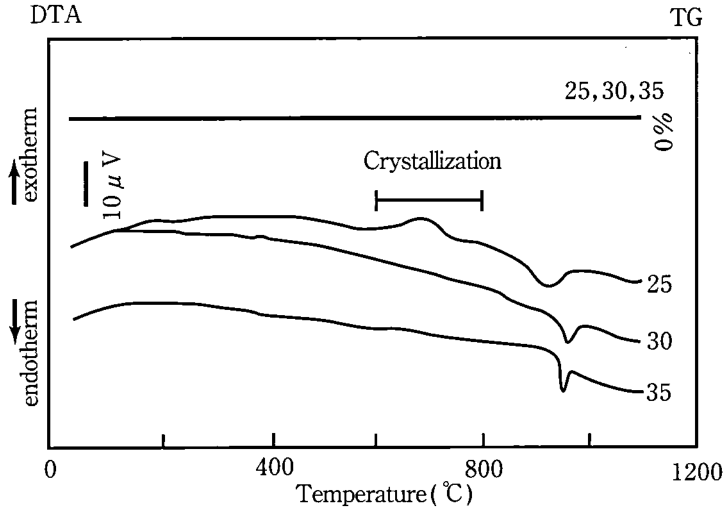

Figure 3 DTA and TG curves of binary glass ceramics (CaO/P_2O_5 = 25, 30, and 35 wt%) when heated to 1100°C.

(ceramming) of new glass ceramics. Thus, the effect of chemical compositions, especially, Al_2O_3, SiO_2, Na_2O, CaO and P_2O_5, on the thermally-induced decomposition and crystallization were examined.

The effect of Al_2O_3 and SiO_2 in the caolinite mineral as main chemical compositions was examined clearly (Table 1). The addition of caolinite to apatite-based glass ceramic raised the crystallization temperature after the decimposition temperature, because the apatite-based glass ceramic (20 wt% CaO/10 wt% P_2O_5/10 wt% MgO/10 wt% Al_2O_3/50 wt% SiO_2) showed glass transition temperature (700° C), crystallization temperature (around 890° C) and melting (endotherm) temperature (around 1200° C)[10]. The additives of sodium silicates were not related to the crystallization of the ceramic powders, because three decomposition temperatures (TE1, TE2, TE3) were found on DTA curves (Tables 2, 3). These characteristic temperatures were observed, although there occurred the crystallization temperature range in feldspathic and aluminous control samples (Table 4). From these DTA results, two main compositions, CaO and P_2O_5, can be selected for new glass ceramics as a future work.

The ceramming (crystallization) procedures were considered by the follow cases. First, the melting (TE3) occurred around 1000° C associated with thermal decomposition (TE2) (Fig 1). After this phenomena at TE2 temperature, the crystallization will occur and then the new glass ceramics are produced, as in Table 1. Secondly, the crystallization occurred between TE1 and TE3 temperaures (Figs 2, 3). These results suggest that new glass CaO/P_2O_5 ceramics can be formed around 400° C for 5 to 20 wt% CaO and also around 800° C for 25, 30 and 35 wt% CaO, as shown in Figs 2 and 3. The reason is that the exthothermic peaks are found between TE1 and TE3 peak temperatures, similar to crystallization peak temperature (TC) in Fig 1 (Table 1). On TG curves, the weight losses in binary glass ceramics with higher CaO percent (25, 30, and 35 wt%) were nor found (Fig 3). This study suggests that the range of CaO percent in the amorphous glass ceramics is limited and the matrix has the crystals after the ceramming of glass matrix in newly-designed ceramic composites.

SUMMARY

To develop functional binary glass ceramics for dental purpose, three types of powders, caolinite, liquid sodium silicate and solid sodium silicate were mixed and their characteristic temperatures were examined by DTA and TG analyses. There appeared three different endothermic temperatures in the powder mixtures to apatite-based glass ceramic, and an exothermic reaction in caolinite-included powders. Based on their thermal behaviours, the effects of chemical compositions on thermal decomposition and crystallization were clearly found and then CaO/P_2O_5 powder mixtures were selected. The peak temperature range of crystal formation in binary CaO/P_2O_5 ceramics with 25, 30, and 35 wt% CaO was detected as an exothermic peak before the thermal decomposition. This suggests that the synthesis condition of CaO/P_2O_5 glass ceramics can be obtained clearly by examining crystal types during crystal formation.

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