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Thermoanalytical Characterization of Dental Porcelains and Kaolinite/Feldspar Minerals

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ABSTRACT

This study examined thermal properties of dental porcelains and kaolinite/feldspar mineral powders by means of differential thermal analysis (DTA) and thermogravimetry (TG), which clarified glass-transition temperature (T_g), dehydration temperature (T_d) and crystallization temperature (T_c) or melting temperature (T_m) in DTA curves and weight loss in TG curves. And also the magnitude of activation energy for dehydration (E_d) and crystallization (E_c) was calculated for their powders. Dental porcelains as $SiO_2/Al_2O_3/K_2O/Na_2O$-based ceramics had a wide range of T_g (190.2 to 352.0°C), T_d (514.4 to 704.0°C) and T_c (930.0 to 1071.7°C) when heated at 40°C/min. Their values increased linearly with increasing a heating rate. Kaolinite/feldspar mineral mixture also showed a wide range of T_g and T_d. T_c temperature was found only for pure kaolinite, and T_m temperature was about 1270°C. The kaolinite/feldspar mixtures had a very weak peak indicating T_c temperature and also more than 1350°C as T_m. The magnitude of activation energy E_d and E_c in dental porcelains respectively ranged from 8.0 to 47.9 kcal/mol and from 13.8 to 116.2 kcal/mol. E_d value was 8.0 to 41.1 kcal/mol in the mixture kaolinite/feldspar. The activation energy result shows that the addition of feldspar to kaolinite decreases the magnitude and exhibites lower E_d value of dental porcelains.

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INTRODUCTION

Dental porcelains are mainly composed of feldspar, kaolinite, potash silicate and dehydrated borax[1,2]. The chemical composition was thus considered in the leucite zone of $SiO_2/Al_2O_3/K_2O$ phase diagram[3]. The dental porcelains also contained a wide variety of frits and fluxes. The dental porcelains were thermally fired at higher test temperatures, so their minerals affected thermal characterization in dental porcelains[4,5]. The feldspar ($K_2O/Al_2O_3/6SiO_2$) and kaolinite ($Al_2O_3/SiO_2/2H_2O$) mixtures in the leucite zone were thus important parameters to thermoanalytical characterization. As a mineral composition[6], dental porcelain ceramics were constituted by high content of feldspar and low contents of kaolinite. In this study dental porcelains and kaolinite/feldspar mineral mixtures were examined by DTA and TG measurement in order to clarify thermal characterization of glass-transition, dehydration and crystallization or melting temperatures.

MATERIALS AND METHODS

Table 1 indicates five types of dental porcelains with different shades investigated, and Table 2 indicates chemical compositions and their mineral percentages (mean) of dental porcelains. Their compositions were SiO_2 (50 to 64 wt%), Al_2O_3 (12 to 18), K_2O (8 to 11), Na_2O (4 to 8), MgO (not-detected to 6), SnO_2 (not-detected to 12), B_2O_3 (not-detected to 5) and other oxides (residual). Their percentages in dental porcelains were measured by ICP analysis (high frequency plasma analysis) at Hiroshima City Kougyou Gizyutsu Center (Hiroshima).

The kaolinite/feldspar mixtures used in this study were 30/70, 50/50 and 70/30, and also both pure kaolinite and feldspar minerals were tested.

The thermoanalytical testing of the samples was carried

Table 1 Dental porcelains tested.

Code		Materials		
		Shade	Brand name	Manufacturer
1	1-1	A_4	Ceramco V.P.G.	Ceramco Inc, NY
	1-2	D_2		
2	2-1	OA_4	Ceramibond	GC, Tokyo
	2-2	DA_4		
3	3-1	A_2	Jelenko P	J.F. Jelenko & Co, NY
	3-2	A_4		
4	4-1	A_2O	Unibond	Shofu Inc, Kyoto
	4-2	A_4B		
5	5-1	513	Vita VMK 68	VITA, Säckingen
	5-2	A_3		

Table 2 Chemical composition in dental porcelains tested.

Code	Composition (wt%)							
	SiO_2	Al_2O_3	K_2O	Na_2O	MgO	SnO_2	B_2O_3	Others
1-1	63	12	8	4	6	12	—	R*
1-2	62	14	11	8	6	—	—	R
2-1	50	18	9	6	—	8	5	R
2-2	63	18	9	7	—	—	5	R
3-1	63	13	8	5	0.5	—	1	R
3-2	63	13	8	6	0.5	—	1	R
4-1	51	18	9	5	—	7	4	R
4-2	64	18	9	6	—	—	4	R
5-1	63	15	8	5	0.5	—	2	R
5-2	64	15	9	5	0.4	0.5	2	R

*R; residual percentage

out using thermal analysis equipment (Shimadzu DT-30, Shimadzu Co, Kyoto). At heating rates of 40, 50 and 60°C/min (atmosphere with a flow of N_2 gas at 3 mL/min), the samples were heated from room temperature (22°C) to 1350°C. Tg (glass-transition temperature), Td (dehydration temperature) and T_c (crystallization temperature) were examined by DTA analysis. Instead of T_c, T_m value was obtained for pure feldspar material melted.

The magnitude of activation energy for dehydration and crystallization was calculated according to Arrhenius plot[7,8,9].

RESULTS

Fig. 1 shows DTA curves as a typical example of code 1-2 material at 40, 50 and 60°/min, representing that T_g, T_d and T_c temperatures were found. Table 3 indicates thermal characteristic temperatures T_g, T_d and T_c in dental porcelains tested at each heating rate of 40, 50

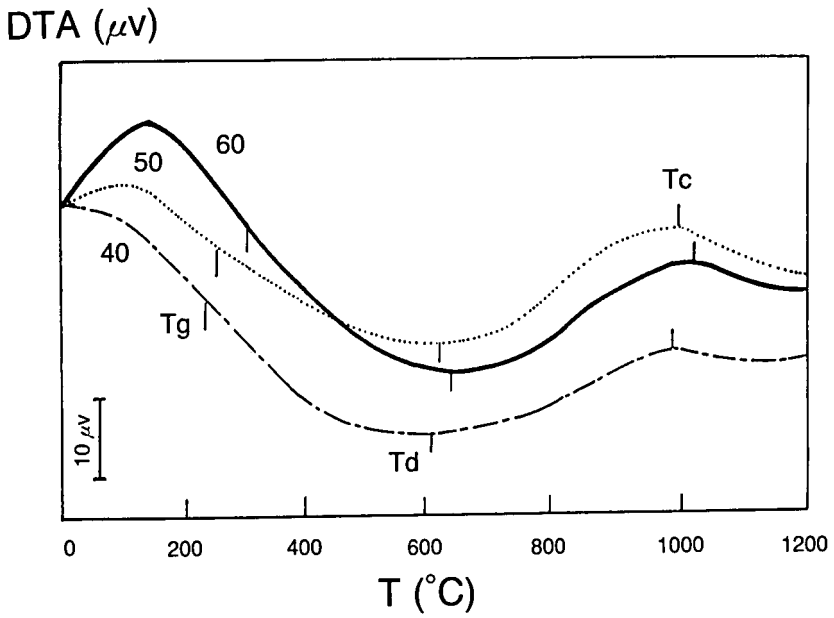


Figure 1 Examples: DTA curves at each heating rate, 40, 50 and 60°C/min (code 1-2). See text for key.

Table 3 Characteristic temperatures (°C) T_g, T_d and T_c in dental porcelains. See text for key. The value shows the mean value.

Code	T_g (°C)			T_d (°C)			T_c (°C)		
	40	50	60	40	50 (°C/min)	60	40	50	60
1-1	241.0	312.3	330.0	624.7	669.5	719.0	974.8	985.0	997.7
1-2	233.7	247.7	301.7	610.2	634.4	650.0	989.0	1001.7	1016.3
2-1	290.7	306.3	298.7	655.3	660.3	672.2	930.0	951.0	954.0
2-2	332.3	357.0	401.0	671.7	687.3	688.3	981.7	999.3	1015.0
3-1	204.0	301.7	335.7	658.3	665.3	673.3	1071.7	1096.7	1128.3
3-2	352.0	372.3	404.7	655.3	693.3	733.0	956.3	1007.3	1052.3
4-1	202.8	205.7	203.0	704.0	742.3	757.3	1002.3	1006.7	1013.7
4-2	262.7	309.0	326.0	643.3	698.3	735.7	1026.7	1037.0	1073.0
5-1	238.7	270.0	285.7	603.2	633.3	641.7	1045.0	1055.0	1076.7
5-2	190.2	215.7	241.7	514.4	529.0	538.3	1047.7	1059.7	1085.0

and 60°C/min. Mean value of T_g ranged from 190.2 to 352.0°C, and T_d ranged from 514.4 to 704.0°C and T_c from 930.0 to 1071.7°C (40°C/min). The increased values were obtained when heated at higher heating rate.

Figs. 2 (a) and (b) show DTA and TG curves of pure kaolinite and feldspar mineral materials, representing that there appear characteristic temperatures T_g, T_d and T_c or T_m. After reaching to T_g temperature (Fig. 2 (a)), weight loss occurred around T_d temperature, and the crystallization formed around 1000°C (T_c). On the contrary, pure feldspar melted at T_m when heated to around 1350°C. Fig. 3 also shows DTA curves of 30/70, 50/50 and 70/30 mixtures at 40°C/min. The mixture showed T_g and T_d temperatures in DTA curves, but a very weak crystallization might occur after reaching to T_d temperature. In this study T_c temperature was not written in Table 4. The characteristic temperatures in DTA curves at 40, 50 and 60°C/min for pure kaolinite and feldspar, 70/30, 50/50 and 30/70 (kaolinite/feldspar) mineral mixture were indicated in Table 4. T_g temperature of 70/30, 50/50 and 30/70 samples ranged from 193.3 to 283.3°C (40°C/min) and the T_d temperature 792.7 to 887.3°C. The values increased at higher heating rates.

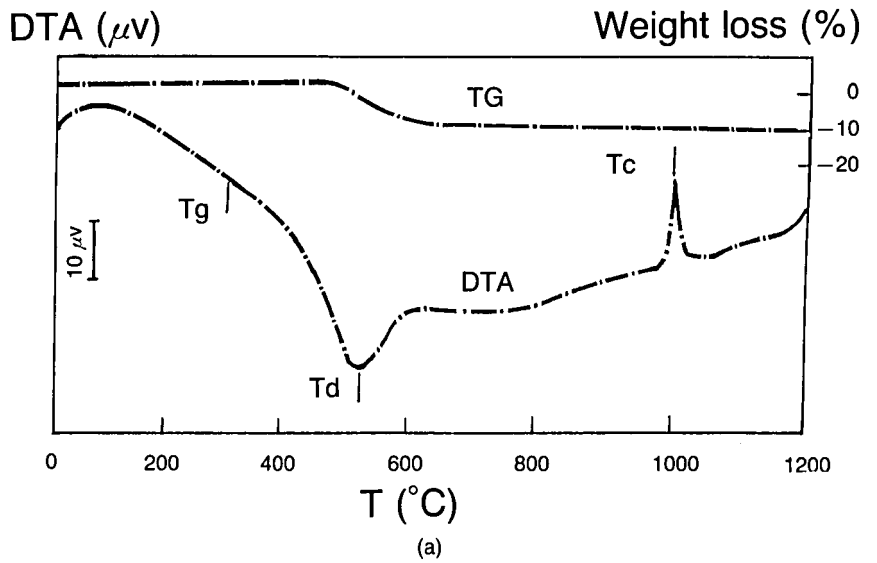
Table 5 indicates the magnitude of activation energy for dehydration and crystallization for dental porcelains. The values were from 8.0 to 47.9 kcal/mol (E_d) and 13.8 to 116.2 kcal/mol (E_c). In Table 6 (the mineral materials) activation energy E_d was 8.0 to 9.8 kcal/mol (70/30, 50/50, 30/70 and feldspar) and 41.1 kcal/mol (kaolinite).

DISCUSSION

Thermal characterization of dental porcelains had T_g, T_d and T_c temperatures, representing that there appeared the firing proceeding at more than 900°C as indicated in T_c values (Table 3). Their characteristic temperatures depended upon the content of feldspar within kaolinite/feldspar mineral mixtures (Table 4). And also the activation energy for dehydration (E_d) ranged from 8.0 to 9.8 kcal/mol, showing smaller values in the mixtures than pure kaolinite (41.1 kcal/mol, Table 6).

Considering the decrease of E_d due to the addition of feldspar in the kaolinite/feldspar mixture, it was deduced that dental porcelains with low E_d value (8.0 to 16.9 kcal/mol) contained larger amounts of feldspar than the others (Table 5). The formation of leucite crystal was also observed for some dental porcelains including feldspar minerals heated at 1100°C for 4 hr[10]. The effect of additive compounds such as B_2O_3 and SnO_2 to dental porcelain ceramic on the formation was remarkably observed[11]. In the present study experimental mineral mixtures had no such additives, so the formation was not found (Fig. 3). Fairhurst et al[12] reported that Tg temperature in dental porcelains changed from 500 to 700°C with increasing heating rates. Natural logarithm of heating rate to reciprocal of T_g temperature was linear[12,13]. Thus, the heating rate dependence of Tg was shown for DTA results.

The heating rate dependence of T_g was observed for the mineral materials tested, and the dependences of T_d and T_c, or T_m were also obtained (Tables 3 and 4). The



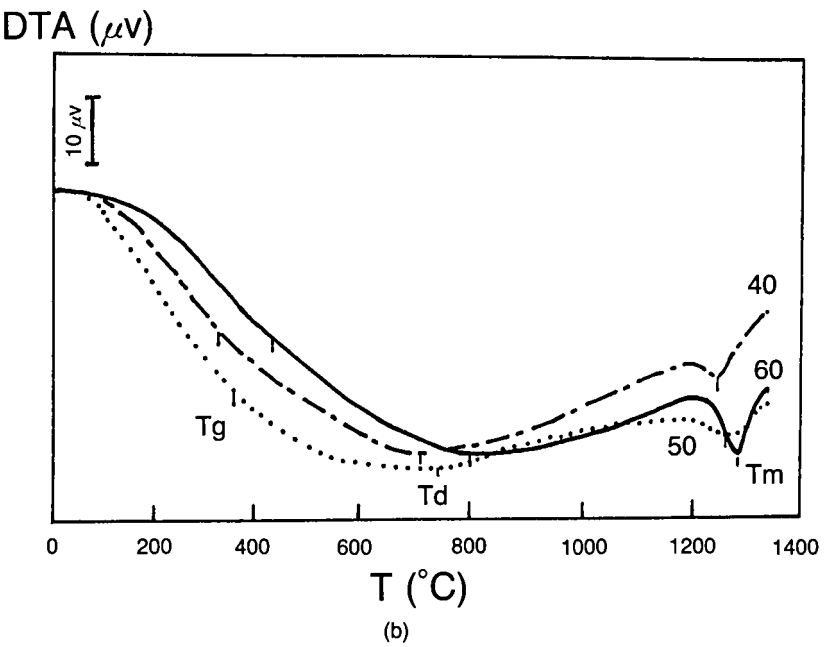


Figure 2 DTA and TG curves of pure kaolinite at 40°C/min (a) and pure feldspar at each heating rate (40, 50, 60°C/min) (b). See text for key.

crystals in dental porcelains were detected when heated to 1350°C (Fig. 1). These results show that the nucleation of crystalline occurs within dental porcelains during firing to higher temperature and/or when heated to more than 900°C.

In this study the temperature for leucite formation in pure kaolinite was about 1000°C, but the addition of pure feldspar did not show the crystallization in the mineral mixtures (Table 4). As reported already[15], experimental SiO_2-based ceramic showed the formation of two crystals (hydroxyapatite and diopside) and also the melting behaviour at about 1200°C. The results suggest that the crystalline type and its amount within as-cast samples are controlled by the additive types and thermal treatment.

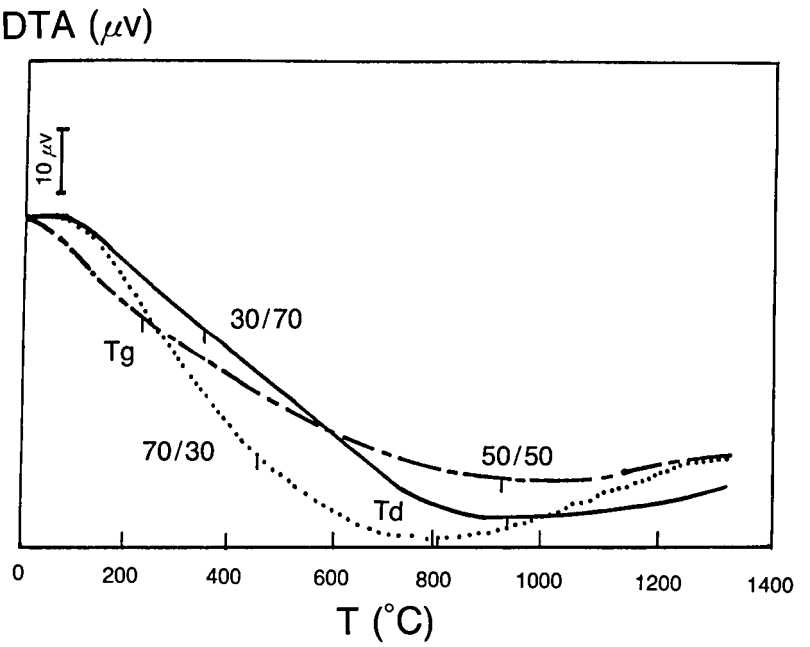


Figure 3 DTA curves of kaolinite/feldspar minerals (40°C/min). See text for key.

Table 4 Characteristic temperatures in kaolinite/feldspar minerals tested. See text for key.

Materials	T_g (°C)			T_d (°C)			T_c (°C)		
	40	50	60	40	50	60	40	50	60
Kaolinite	396.5	427.5	466.7	530.0	537.3	543.0	1008.5	1011.5	1016.0
70/30	283.3	448.7	552.0	792.7	836.0	916.5	—	—	—
50/50	194.3	223.0	311.7	846.7	895.9	993.7	—	—	—
30/70	223.7	328.7	359.7	887.3	929.7	1025.0	—	—	—
Feldspar	325.0	371.0	436.3	712.0	742.0	797.8	1267.7*	1274.2*	1279.7*

*T_m; melting temperature. 40, 50, 60; heating rate.

Table 5 Activation energy for dehydration (E_d) and crystallization (E_c) in dental porcelains. See Table 1 for code.

Code	Activation energy	
	E_d	E_c
1-1	15.6	56.5
1-2	15.1	49.3
2-1	42.8	50.8
2-2	42.8	40.7
3-1	47.9	26.2
3-2	9.7	13.8
4-1	15.2	116.2
4-2	8.0	90.4
5-1	16.9	41.1
5-2	12.9	32.1

(kcal/mol)

Table 6 Activation energy E_d in kaolinite/feldspar minerals.

Materials	Activation energy
	E_d
Kaolinite	41.1
70/30	8.5
50/50	8.0
30/70	9.0
Feldspar	9.8

(kcal/mol)

SUMMARY

Dental porcelains showed T_g and T_d as glass-transition temperature and dehydration temperature, and also exhibited crystallization temperature of more than 1000°C. In case of the mixture of kaolinite/feldspar the same characteristic temperatures as dental porcelains were observed. The magnitude of activation energy for dehydration and crystallization ranged from 8.0 to 47.9 kcal/mol and 13.8 to 116.2 kcal/mol, resspectively, in dental porcelains tested. The value of activation energy for dehydration was smaller in the kaolinite/feldspar mixture than in pure kaolinite mineral. The increase in the amount of kaolinite exhibited higher melting temperature (T_m) than that in mineral material feldspar, but glass-transition temperature (T_g) was smaller than those of pure mineral materials. Thus, appropriate amounts of minerals as additives to glass ceramics can control glass-transition temperature and the formation of crystalline within as-cast sample. These results can apply to the manufacturing of experimental SiO_2-based dental porcelains or glass ceramics.

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