

Glass Transition Temperatures of Dental Porcelains Determined by DSC Measurement

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The differential scanning calorimetry (DSC) curves for three commercial dentin and incisal porcelains fused-to metal were measured using high-temperature DSC. The glass transition temperatures (T_g) were determined from the DSC curves at heating rates of 7 – 20°C/min, and the activation energy was derived from an Arrhenius plot of negative reciprocal T_g vs. logarithm of heating rate. The T_g of the dental porcelains depended on the content of aluminum oxide, whereas the activation energy depended on the content of sodium oxide. The ultra-low fusing type porcelains had a low activation energy due to the higher content of sodium oxide than the other porcelains.

Key words : Glass transition temperature, Dental ceramics, Differential scanning calorimetry

INTRODUCTION

Glass transition temperature (T_g) data for dental porcelains are useful in the evaluation of stress generation during the firing process. The stress begins to develop at T_g , and temperature stress relaxation does not occur below T_g . In the case of porcelain fused-to metal, the stress at any temperature (T) below T_g is directly proportional to the differences in thermal contraction changes of the two materials from T_g to T . Fairhurst *et al.*¹⁾ measured the T_g of various dental porcelains using a beam bending viscometer. Twiggs *et al.*^{2,3)} also measured the T_g of dental porcelains at high heating rates, using the same methods.

On the other hand, differential thermal analysis (DTA) has been used previously to determine the T_g of glass and ceramics, because the required temperatures were in the upper limits of the usable temperature range for differential scanning calorimetry (DSC). However, a high-temperature type DSC instrument was recently developed, offering temperatures up to 1500°C. It is expected that DSC measurement would yield more precise and useful data than DTA, because of its higher sensitivity and ability to directly indicate heat capacity data. The purpose of this study was to use high-temperature DSC to determine the T_g and activation energy of a number of porcelains, and to discuss the thermal behavior of porcelains around T_g .

Table 1 Porcelains used in this study

Code	Name	Manufacturer	Type	shade	Lot No.
VB	Vintage	Shofu	Body	A3B	079573
VI	"	"	Incisal	59	079558
DD	Deguceram Gold	Degussa	Dentin	A3	01
DI	"	"	Incisal	3	01
CD	Carrara	Elephant	Dentin	A3	7955
CI	"	"	Incisal	59	7960

MATERIALS AND METHODS

Three dentin and three incisal porcelain powders were used without modification in this study. The brand names and manufacturers are listed in Table 1. The DSC curves were measured using a high-temperature DSC instrument (Rigaku, DSC 8270, Tokyo, Japan) with a platinum sample pan and pure Al₂O₃ powders as a standard. The weights of specimen and standard powders were about 20 mg. Heating rates of 2, 5, 7, 10, 12, 15 and 20°C/min from room temperature to 1000°C in air were applied. From the observed DSC curve, *T_g* was determined by manually drawing additional straight lines for each endothermic step. The measurements were repeated three times for each condition.

Moynihan *et al.*⁴⁾ reported that the activation energy Δh^* for *T_g* can be derived from the regression line in an Arrhenius plot of negative reciprocal *T_g* vs. logarithm of heating or cooling rate, *q*, as follows.

$$d \ln |q| / d(1/T_g) = -\Delta h^*/R$$

where *R* is the gas constant. The negative reciprocal of the observed *T_g* values for each dental porcelain powder was then plotted against the logarithm of the heating rates. From these Arrhenius plots, linear regression lines were obtained by the least squares method, and the activation energies were calculated by the slope of the regression lines.

According to the manufacturers directions, the disc-shape specimens were fired at 940°C for VB and VI, 780°C for DD and DI, and 845°C for CD and CI, and were ground from 120-grit to 1000-grit papers and polished with 1-μm and 0.3-μm alumina powder. The chemical composition of the polished surfaces was determined using an energy-dispersive X-ray micro-analyzer (EDX) (JEOL, JED-2110X, Tokyo Japan). As these EDX results include both the glass matrix and leucite crystal phase (K₂O·Al₂O₃·4SiO₂), the composition of the glass matrix was derived by subtraction of the leucite crystal content determined by an X-ray diffraction study (XRD)⁶⁾.

RESULTS AND DISCUSSION

Fig. 1 shows the DSC curves for the six porcelains measured at a heating rate of 20 °C/min. The *T_g* values were around 550°C for VB and VI, 480°C for DD and DI, and

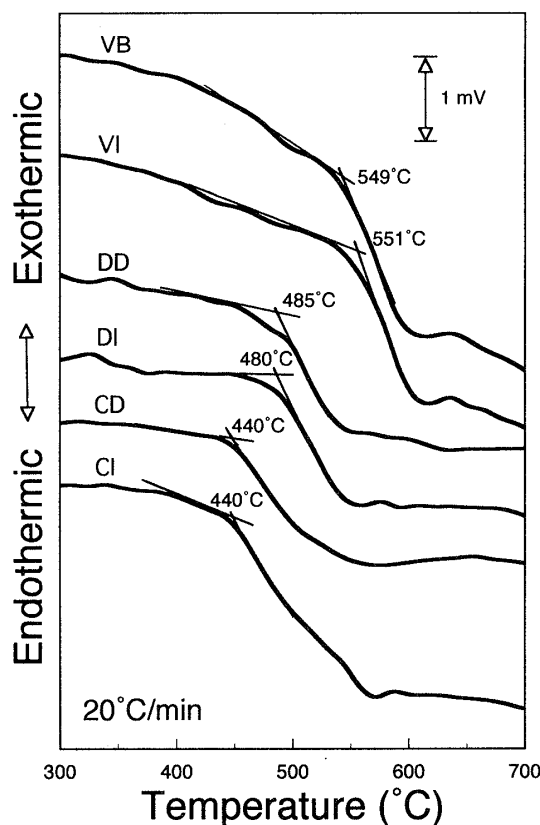


Fig. 1 DSC curves for six dental porcelains measured at a heating rate of 20°C/min. Figures stand for T_g .

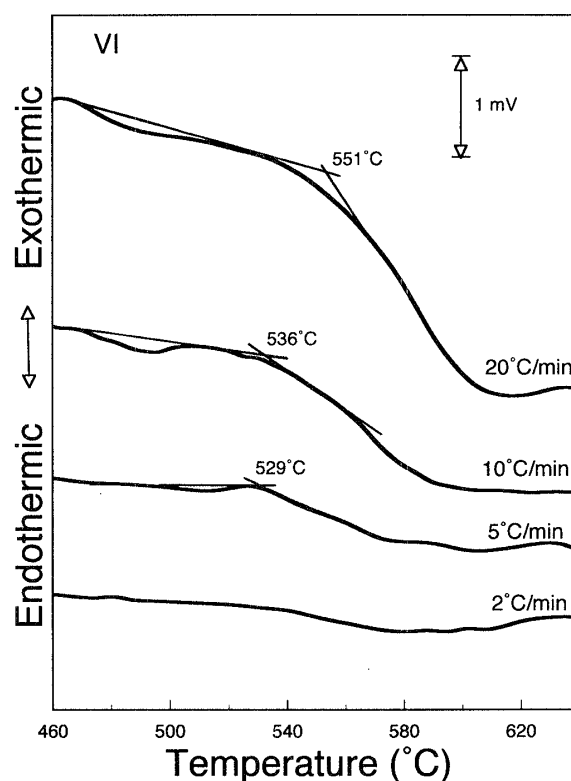


Fig. 2 DSC curves for VI measured at the heating rates of 2, 5, 10 and 20°C/min. Figures stand for T_g .

440°C for CD and CI. There was no remarkable difference between the DSC curves of body and incisal of each brand. Fig. 2 shows the DSC curves for VI measured at the heating rates of 2, 5, 10 and 20°C/min. It was found that both T_g and capacity change increased with the heating rate. However, it was difficult to find clear steps for reliable measurements of T_g from the curves obtained at 2 and 5°C/min. Therefore, only the T_g values obtained among 7–20°C/min were used for the following analysis.

Fig. 3 shows the relationship between the T_g and the heating rates. The T_g values were in the range of 520–560°C for VB and VI, 445–490°C for DD and DI, and 410–445°C for CD and CI. Furthermore, the values of T_g for all porcelains had a tendency to increase with the heating rate. Fig. 4 shows the Arrhenius plots of negative reciprocal T_g vs. logarithm of heating rates. Each point is the mean value of the three measurements. Linear regression analysis of these data showed regression coefficients of 0.71–0.97. Fig. 5 shows the activation energies calculated by the slopes of the regression lines for the six porcelains. The activation energies are 594–687 kJ/mol for VB, VI, CD and CI, 363 kJ/mol for DD and 383 kJ/mol for DI. DD and DI showed rather smaller values than the others, suggesting that the T_g of these porcelains is more dependent on the heating rate. Twiggs *et al.*^{2,3)} reported that the

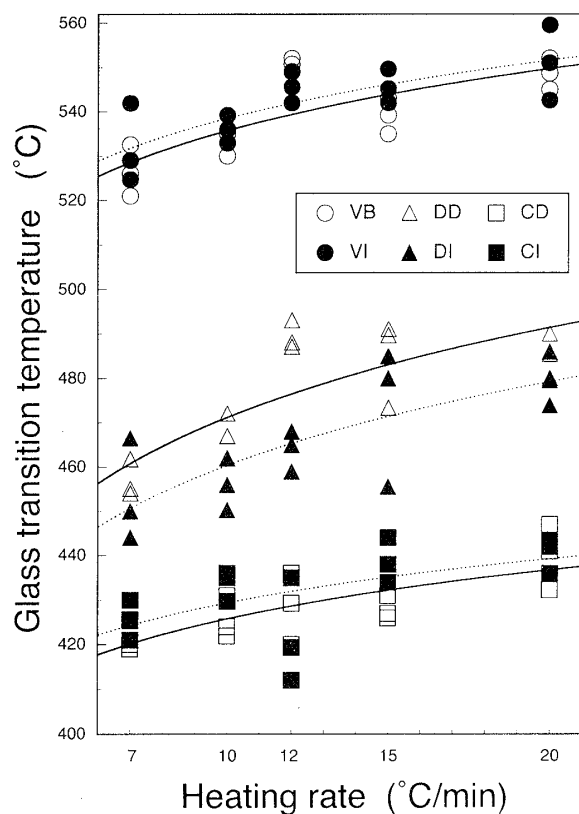


Fig. 3 Plot of T_g against heating rates for the six dental porcelains.

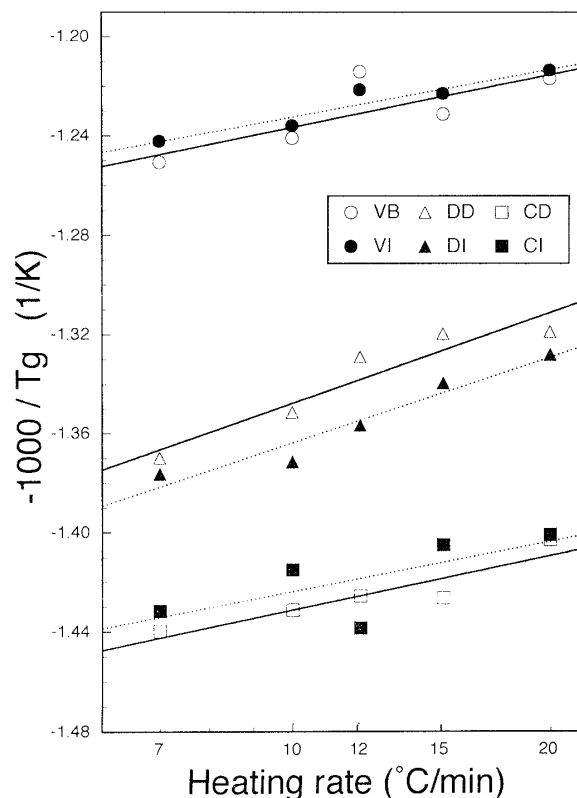


Fig. 4 Arrhenius plots of negative reciprocal T_g vs. logarithm of heating rates for six dental porcelains.

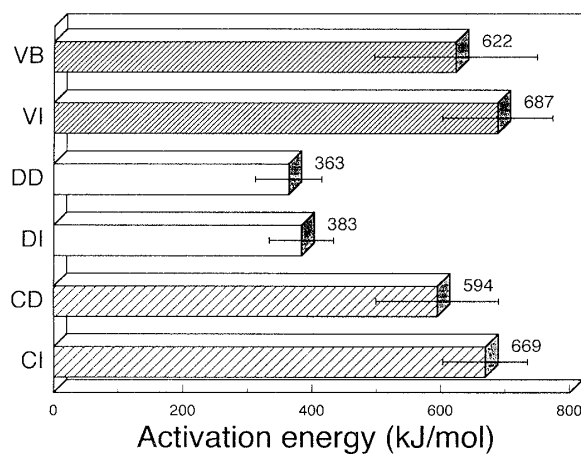


Fig. 5 Activation energies for six dental porcelains. Error line indicates $t(\phi_e, 0.05)$.

Arrhenius-type relationship between T_g and heating or cooling rates was maintained into the high-temperature range. Moynihan *et al.*^{4,5)} further reported that this activation energy is essentially equal to the activation energy for viscous flow. Therefore, it is concluded that the temperature-dependency of the viscous flow of DD and DI is

higher than for the other porcelains studied.

Twiggs *et al.*³⁾ reported the activation energy for body porcelains and opaque porcelains obtained using the bending beam technique to be 82–153 kcal/mol (=342–641 kJ/mol) and 82–148 kcal/mol (=343–619 kJ/mol), respectively with no significant difference between them. However, they did not discuss the relationship between T_g and the activation energy, or the relationship between these thermal properties and composition.

Table 2 shows the chemical composition of the fired porcelains determined by EDX, the content of leucite crystal determined by XRD⁶⁾, and the calculated composition of the glasses. Sodium, potassium, aluminum, and silicon were the main components of these porcelains, with no other elements detected. Although these fired porcelains consist of leucite crystal particles and a glass matrix, it is quite difficult to quantitatively analyze the chemical composition of each component. The composition of the glass was derived from the data of the composition of the fired porcelains and the content of leucite crystal determined by XRD⁶⁾.

Table 3 shows the regression coefficients between the content of oxides in the glass matrix and T_g at 10°C/min and/or activation energy. The regression coefficient between T_g and the content of aluminum oxide, and between the activation energy and the content of sodium oxide, showed the highest values, 0.980 and -0.963 , respectively. Fig. 6 shows the scatter graphs of these relationships. It was found that T_g increased with the contents of aluminum oxide, while the activation energy decreased with the content of sodium oxide. The regression coefficients between T_g and the

Table 2 Composition of porcelains (wt%)

	Composition of fired porcelain				Content of Leucite	Composition of glass			
	Na ₂ O	K ₂ O	Al ₂ O ₃	SiO ₂		Na ₂ O	K ₂ O	Al ₂ O ₃	SiO ₂
VB	6.7	11.6	18.5	63.3	22.0	8.6	8.8	17.1	65.5
VI	7.3	10.0	19.2	63.5	21.7	9.2	7.0	18.1	65.7
DD	11.4	10.7	15.2	62.7	16.1	13.6	8.6	13.6	64.2
DI	12.4	10.1	14.3	63.3	14.5	14.5	8.1	12.7	64.7
CD	7.2	13.8	13.5	65.5	25.2	9.6	11.2	10.2	69.0
CI	6.2	13.3	14.8	65.7	22.3	8.0	10.9	12.4	68.8

Table 3 Regression coefficients between content of oxides in the glass matrix and thermal properties of dental porcelains.

Oxide	T_g	Activation energy
Na ₂ O	-0.213	-0.963
K ₂ O	-0.762	0.220
Al ₂ O ₃	0.980	0.330
SiO ₂	-0.545	0.629
Na ₂ O+K ₂ O	-0.703	-0.878
(Na ₂ O+K ₂ O)/Al ₂ O ₃	-0.918	-0.525

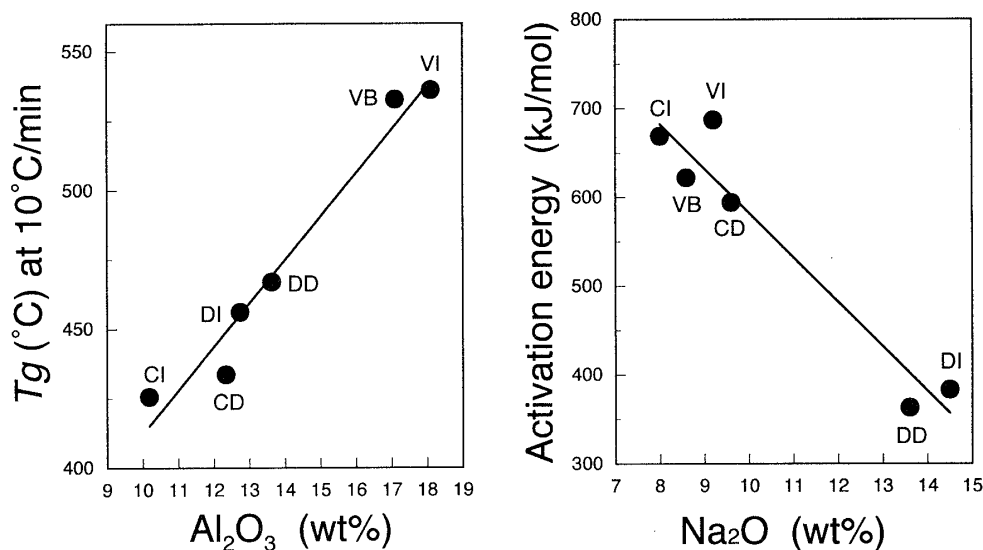


Fig. 6 Plot of T_g at 10°C/min against content of aluminum oxide (left) and activation energy against content of sodium oxide (right).

contents of alkaline oxides were lower, as shown in Table 3. It is known that trivalent aluminum ions act as a network former in glass, thus increasing the viscosity, surface hardness and strength as well as reducing the thermal expansion⁷⁾. It was thus concluded that VB and VI have higher T_g than the other porcelains, because of their higher content of aluminum oxide.

According to a patent⁸⁾, DD and DI may consist of SiO₂ 60–65 wt%, Al₂O₃ 8.5–11 wt%, K₂O 8–12 wt%, Na₂O 10.5–12 wt%, CaO 0.7–2 wt%, BaO 0.6–2 wt%, B₂O₃ 0.5–2.5 wt%, Sb₂O₃ 0.1–0.6 wt%, CeO₂ 0–0.5 wt%, TiO₂ 1.2–3.8 wt%, Li₂O 0.8–1.4 wt% and F₂ 1.2–3.8 wt%, and their glass transition temperatures are about 450°C. In the case of the patent assumed for CD and CI⁹⁾, the porcelain may be prepared by mixing (a) a high content of leucite (50–80 wt%) with (b) glass frits (5–45 wt%) and (c) low-fusing glass frits (5–15 wt%). The chemical composition seems to be (a) Al₂O₃ 15–20 wt%, K₂O 13–19 wt%, Na₂O 0–5 wt%, and both SiO₂ and other additives balanced, (b) Al₂O₃ 10–15 wt%, K₂O 4–7 wt%, Na₂O 6–15 wt%, BaO 0–3 wt%, Li₂O 0–3 wt%, and both SiO₂ and other additives balanced, and (c) Al₂O₃ 0–5 wt%, K₂O+Na₂O 12–30 wt%, BaO 0–5 wt%, Li₂O 0–5 wt%, and both SiO₂ and other additives balanced. Although the EDX employed in this study can measure all these elements according to the manufacturers specifications, only O, Si, Al, K and Na could be observed precisely. It seems that the contents of the other elements in the porcelains were insufficient to be detected by the EDX transducer. In spite of these analytical problems, the T_g of porcelain strongly depends on the content of aluminum oxide, suggesting that these other elements are added to improve other properties such as thermal expansion and chemical durability.

On the other hand, it was confirmed that the activation energy decreases with the content of sodium oxide, as shown in Fig. 6. It is known that the modifier oxides such as sodium and potassium oxides disrupt Si–O bond linkages, resulting in a less

rigid structure, and it is therefore concluded that DD and DI have lower activation energies than the other porcelains, because of their higher content of sodium oxide.

CONCLUSIONS

The DSC curves for three commercial dentin and incisal porcelains fused-to metal were measured using high-temperature DSC. The T_g values were determined from the DSC curves at heating rates of 7 to 20°C/min, and the activation energy was derived from the Arrhenius plot of negative reciprocal T_g vs. logarithm of heating rate. The chemical compositions of the porcelains were determined using EDX. The T_g of the dental porcelains depended on the content of aluminum oxide, whereas the activation energy depended on the content of sodium oxide. DD and DI had relatively low activation energies due to their higher content of sodium oxide than the other porcelains, indicating different thermal behavior around T_g .

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本号掲載論文の和文抄録

ゾルーゲル法によって調製した50重量%シリカ-20重量%リン酸- 30重量%カルシア組成を有するガラス-セラミックス 粉末の合成特性の評価

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テトラエトキシシラン, 硝酸カルシウム, リン酸水溶液を出発原料とするゾルーゲル法によって50重量%シリカ, 20重量%リン酸, 30重量%カルシア組成を有するガラス-セラミックス粉末を調製し, 合成特性を熱分析, 赤外吸光, X線回折によって調べた. その結果, 以下の知見を得た. (1) 加熱温度を600℃以上にするとゲル体中の側鎖の炭素が脱離し, シリカ系ガラスマトリックス

を形成した. (2) 加熱温度を900℃以上にすると, リン酸カルシウムなど4種類の結晶がガラスマトリックス中に活発に生成した. (3) 加熱温度が900℃以下の場合, 生体親和性を付与する水酸基が多く存在した. (4) 融点は1400℃以上であった. (5) 本研究で得られたリンとカルシウムを含有するシリカ系粉末は生体活性なインプラント材料として使用可能と考えられた.

DSC測定による歯科用陶材のガラス転移温度

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3種の金属溶着用市販歯科用陶材 (Vintage, Carrara, Deguceram gold) のデンチンおよびインサイザルのDSC曲線を高温型DSCにより測定した. 7~20℃/minの昇温速度で測定したDSC曲線よりガラス転移温度 (T_g) を求め, T_g と昇温速度とのアーレニウス・プ

ロットより活性化エネルギーを求めた. 歯科用陶材のT_g は酸化アルミニウムの含有量に依存し, 活性化エネルギーは酸化ナトリウムの含有量に依存した. Deguceram goldは他の陶材より酸化ナトリウム含有量が高いため低い活性化エネルギーを示した.

ガラス相へのNa₂O添加がリユーサイト結晶を 含む陶材の強度へ及ぼす影響

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陶材をリユーサイト結晶により強化する場合に有効な地のガラス相の性質について調べた. 実験試料としてNa₂Oの量が異なる5種の長石ガラスに, 高純度天然リユー

サイト結晶を0, 20, 40%混合した複合陶材 (15種類) を用意した. そして, ガラス相とリユーサイトの熱的性質, 各陶材試料の3点曲げ強さを測定した. その結果,