JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 1 (1990) 207–210

A thermoanalytical study on non-asbestos ring-lining materials for dental application

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New non-asbestos papers composed of glass fibres and ceramic fibres were used as asbestos-substitute casting-ring liners in the dental field. The lining materials showed a softening temperature higher (above 800°C) than the furnace temperature. As far as the accuracy due to dimensional changes is concerned, new ring-lining materials such as glass fibre (paper and twill) and ceramic fibre have an effect similar to that of a conventional asbestos paper, indicating that non-asbestos liners could be advantageous.

1. Introduction

In the dental casting procedure, the setting investment is heated within a stainless steel casting ring, and the ring needs dry asbestos lining material which absorbs water readily [1–4]. However, the use of asbestos ring liners could be regarded as a health risk in dental casting [5, 6]. Thus, asbestos as a ring liner has been replaced by alternative materials, such as cellulose paper and ceramic paper [7–9], and the effect of casting-ring liners on the expansion of a gypsum-bonded investment was examined. The expansion is composed of both the setting expansion and the subsequent thermal expansion of the set investment. The investment within the ring is generally heated to 700° C as a burn-out temperature, and therefore the ring liner has to be highly heat-resistant. The casting-ring liners also have a cushioning effect within the stainless steel ring during setting and thermal expansion.

In this study new casting-ring liners of different chemical compositions were used for dental application. Provided that the casting-ring liners are used practically, properties such as thermal variation with increasing test temperature are needed. Therefore, thermal analyses were made to determine whether new casting-ring lining materials were suitable for dental casting, and the dimensional change of cast specimens was measured using different casting-ring liners.

2. Materials and methods

The casting-ring liners investigated are listed in Table I, along with their composition system, thickness and manufacturer. Six different ring lining materials were composed of conventional asbestos paper (MgO–SiO_2 system; GC Co., Tokyo, Japan), glass fibres (SiO_2–Al_2O_3–CaO system; supplied by Nippon Electric Glass Co., Shiga, Japan) and ceramic fibre lining materials (Al_2O_3–SiO_2 system; a commercial ceramic fibre (Kaolin) was used (Dentsply Co., York, Pennsylvania, USA) and another ceramic fibre (NEG) was supplied by Nippon Electric Glass Co.) cut from them were analysed by thermal analysis to investigate their use as casting liners in a stainless steel ring in dental casting. The weight (g) per m^2 was obtained as follows: glass fibre (twill), 500; glass fibres (paper and 3T), 200; ceramic fibre (Kaolin), 275; and ceramic fibre (NEG), 200.

For thermal analyses (Shimadzu Co., Kyoto, Japan; DT-30), such as differential thermal analysis (DTA) and thermogravimetry (TG), a sample weight of 3 mg was used with a reference weight (30 mg) of Al_2O_3 powder for each thermal analysis, similarly to in a previous study [10]. In the analyses the glass-transition temperature (T_g), the softening temperature (T_d) and the temperature for mullite formation (T_c) were measured in the ring lining materials. The heating rates for the lining materials were 20, 30 and

TABLE I Casting-ring lining materials used in this study

Material	Composition	Thickness (mm)	Manufacturer
Asbestos paper	MgO–SiO_2	0.75 ± 0.03	GC Co.
Glass fibre	SiO_2–Al_2O_3–CaO		Nippon Electric Glass Co.
Paper		1.35 ± 0.10	
Twill		0.35 ± 0.01	
3T		1.50 ± 0.02	
Ceramic fibre	Al_2O_3–SiO_2		Dentsply Co.
Kaolin		1.00 ± 0.01	Nippon Electric Glass Co.
NEG		1.00 ± 0.02	

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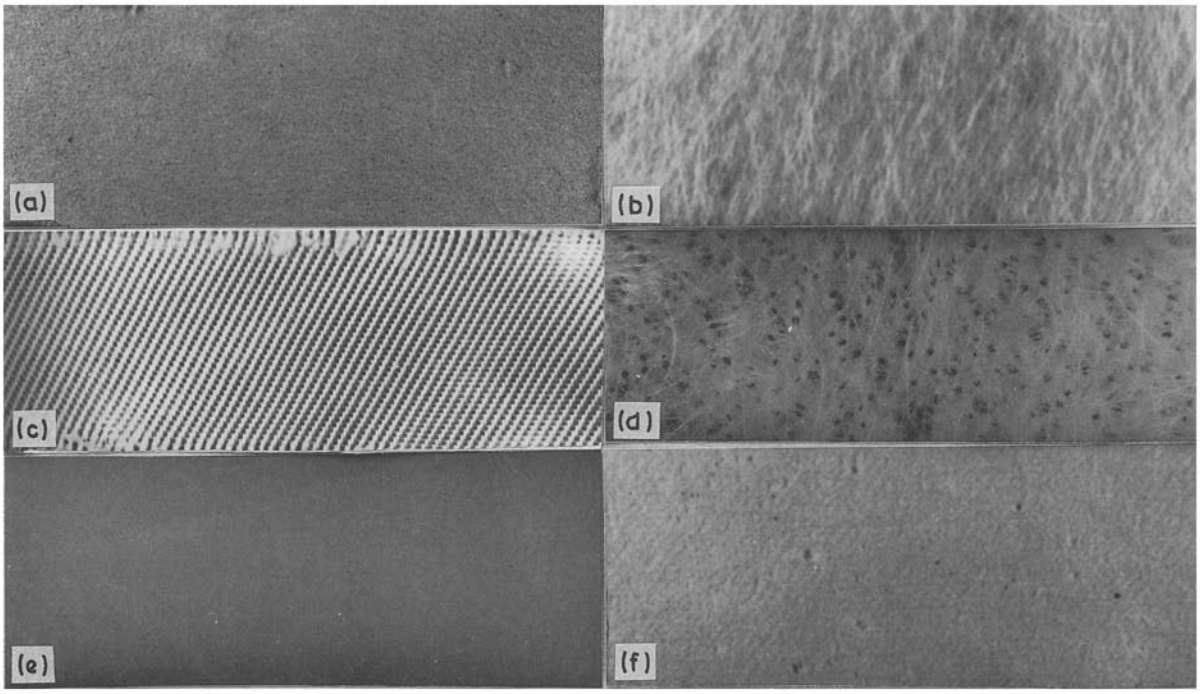

Figure 1 Optical micrographs of casting-ring liners: (a) asbestos paper, (b) glass fibre (paper), (c) glass fibre (twill), (d) glass fibre (3T), (e) ceramic fibre (Kaolin) and (f) ceramic fibre (NEG).

50° C min^{-1} over the temperature range from room temperature to 1000° C, except pure caolinite which was heated to 1200° C. Based on the thermal analyses, the activation energy for glass transition or mullite formation was calculated according to the method reported in [11].

The mould made of a gypsum-bonded investment (cristobalite P, water/powder ratio 0.33; Shofu Co., Kyoto, Japan) set within a stainless steel ring and was then heated to 700°C with the six different ring lining materials being used. The mould was then transferred to a centrifugal casting machine (Castron-8; Yoshida Co., Osaka, Japan) in which the 82.1% Ag–12.0% Cu–1.0% Co–1.1% Si-based alloy was induction-melted (melting temperature 900°C; Serumin Chem. Co., Osaka, Japan; other additive elements: chromium 0.3%; nickel 0.4%; tin 0.6%; indium 0.4%; tantalum 0.5%; iron 0.8%; zinc 0.2%; antimony 0.3%; titanium 0.3%). The metal crowns after casting were examined under sharp light through a magnifying lens (4 ×), and the accuracy of the crowns was calculated from the dimensional change. The value was evaluated by measuring the clearance between the margin of the crown and the shoulder of the stainless steel die for each metal crown (see Fig. 6 in Section 3) [12, 13].

TABLE II T_d at heating rates of 20, 30 and 50° C min^{-1} for the ring lining materials

Material	Heating rate (° C min^{-1})		
	20	30	50
Glass fibre			
Paper	805 ± 1.0	821 ± 2.6	832 ± 2.4
Twill	843 ± 1.4	852 ± 4.3	863 ± 2.4
3T	841 ± 1.3	847 ± 2.2	857 ± 2.4
Ceramic fibre			
Kaolin	n.f.	n.f.	n.f.
NEG	n.f.	n.f.	n.f.

n.f., T_d not found.

3. Results

Fig. 1 shows the lining materials for the stainless steel ring, having the properties given in Table I. Macroscopic observation of the specimen surfaces reveals differences among them (Fig. 1). Fig. 2 shows typical DTA curves for pure caolinite, indicating the three characteristic temperatures T_g, T_d and T_c in their curves (heating rates 40, 50 and 60° C min^{-1}). In the DTA curves each of T_g, T_d and T_c was found with increasing test temperature, and their values increased with increasing heating rate. Figs 3 (glass fibre; paper), 4 (glass fibre; twill) and 5 (ceramic fibre; NEG) show the DTA curves of ring lining materials obtained at heating rates of 20, 30 and 50° C min^{-1}. For non-asbestos liners composed of glass fibres (paper and twill) the T_d temperature, representing a softening of the glass fibres, was found above 800°C at these heating rates, but the crystallization of mullite, which agrees with a peak of exothermic reaction in pure caolinite, took place at about 1000° C for ceramic fibre (NEG). That is, the caolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) decomposed with dehydrating H_2O around 500° C as indicated by T_d, and both mullite ($3Al_2O_3 \cdot 2SiO_2$) and silica (SiO_2) were formed above 980° C [14].

The results in Fig. 2 are summarized as follows: glass fibres softened above 800° C without the

TABLE III T_c of ceramic fibres (for key, see Table I)

Material	Heating rate (° C min^{-1})		
	20	30	50
Ceramic fibre			
Kaolin	938 ± 1.3	955 ± 0.6	989 ± 0.8
NEG	977 ± 0.1	985 ± 0.1	1001 ± 0.1

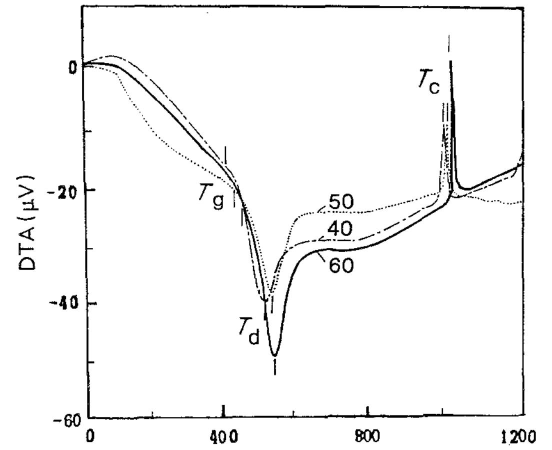

Figure 2 Differential thermal analysis (DTA) and thermogravimetry (TG) curves of pure caolinite at heating rates of 40, 50 and 60° C min^{-1}. T_g, glass-transition temperature; T_d, temperature for softening; T_c, crystallization temperature for a mullite formation.

formation of mullite, whereas ceramic fibre formed a mullite along with SiO_2 at about 1000° C without softening of the ceramic fibre. The change of T_d for casting-ring liners with increasing heating rate is shown in Table II. For three kinds of glass fibres (paper, twill and 3T), T_d increased with increasing heating rate, and was between 800 and 870° C. On the contrary, no T_d was found for the two kinds of ceramic fibres represented by Kaolin and NEG. In Table III T_c for a mullite formation is shown for the above heating rates, showing the increase of T_c with increasing heating rate (the value ranged from 938 ± 1.3 to 989 ± 0.8° C, or from 977 ± 0.1 to 1001 ± 0.1° C).

Table IV shows the activation energy for softening of glass fibres and for mullite formation in ceramic fibres, using the method of the Arrhenius plot described previously [10, 11]. The value was smaller for glass fibre (paper) than for other glass fibres (twill and 3T), but T_d was high compared with the temperature of the gypsum-bonded investment heated to 700° C at a heating rate of about 10° C min^{-1}.

Fig. 6 shows a schematic figure and an example of how to calculate the dimensional change of a metal crown, and Table V shows the value in silver-based alloy when five different casting-ring liners were used to compare the result with that due to asbestos paper, or that without asbestos (for a metal die, A is the diameter of the upper surface (8.90 mm), B is the diameter at the other side (9.89 mm) and H the height of the die (9.92 mm). The taper was 10 from the expression $H/(B - A)$). The clearance was measured on an optical micrograph, and the dimensional change was calculated as [clearance/(taper × B)] × 100. The values in glass fibres (paper and twill; −0.07 and −0.19%) and ceramic fibre (NEG; −0.15%) were larger than those for glass fibre (3T; −0.71%) and ceramic fibre (Kaolin; −0.21%). Their values were also very large compared with the result without asbestos paper (−1.37%). Of the ring lining materials tested, glass fibre (paper) had the largest value.

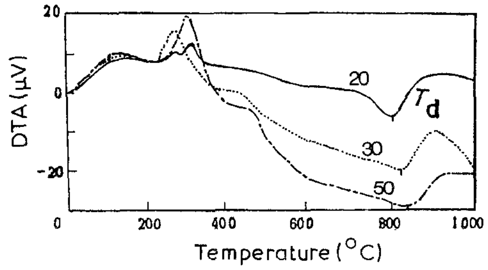

Figure 3 DTA curves at heating rates of 20, 30 and 50° C min^{-1} for non-asbestos liner of glass fibre (paper). T_d denotes the softening temperature.

4. Discussion

From thermal analyses (Figs 2 to 5 and Tables II to IV) it can be seen that a high T_d appeared for casting-ring liners of glass fibres (paper, twill and 3T) and ceramic fibres had no T_d. Compared with the heating rate (about 10° C min^{-1}) of a stainless steel ring in the furnace heated from room temperature to 700° C, T_d for the softening of ring liners was above 800° C. For ceramic fibres as a dry non-asbestos liner, the water uptake of commercial ceramic fibres was very poor compared with conventional asbestos paper [15, 16].

The effect of the heating rate on T_d or T_c for mullite formation was not as large, ranging from 805 to 863° C (Tables II and III). Thus, there may not be a large thermal change with increasing furnace temperature, and the dimensional change of the metal crown was large (Table IV). That is, the value of the dimensional change was −1.37 ± 0.17% when used without asbestos paper, and this means that the shrinkage of the metal crown has to be compared with that of the asbestos-lined ring. The value of the dimensional change when using asbestos paper was considerably larger (−0.21 ± 0.03% as an average value). Table V shows the effect of the non-asbestos liner on the measured dimensional change. Even with glass fibres (paper and twill) and ceramic fibre as the

TABLE IV The values of activation energy for softening (glass fibre) and mullite formation (ceramic fibre) in the ring lining materials (for key, see Table 1)

Material	ΔE (kcal mol^{-1})
Glass fibre	
Paper	75.8
Twill	115.1
3T	139.9
Ceramic fibre	
Kaolin	53.5
NEG	121.3

TABLE V The dimensional change of metal cast crowns using ring lining materials (for asbestos paper the dimensional change was −0.21 ± 0.03%)

Material	Dimensional change (%)
Glass fibre	
Paper	−0.07 ± 0.05
Twill	−0.19 ± 0.04
3T	−0.71 ± 0.16
Ceramic fibre	
Kaolin	−0.21 ± 0.05
NEG	−0.15 ± 0.04

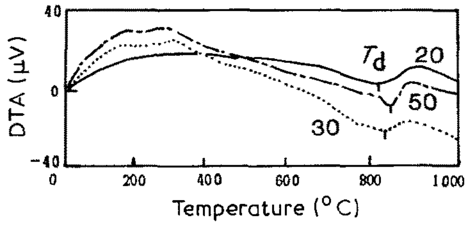

Figure 4 DTA curves of non-asbestos liner (glass fibre; twill) at three different heating rates (for key, see Fig. 3).

casting-ring liner, the dimensional change was greatly increased (to −0.07 or −0.15%), whereas the value of the dimensional change due to the use of glass fibre (3T) had a smaller value (−0.71 ± 0.16%) than that due to the use of asbestos paper (−0.21 ± 0.03%). The largest value in glass fibre (paper) of the liners tested was a better dimensional change. The result shows the possibility of an application as a ring lining material in the dental field. The difference between the dimensional change for the ring liner (glass fibre; paper) with the largest value and with an asbestos liner was significant ($p < 0.01$). When casting-ring liners were used dry, they rapidly absorbed water from the mix, lowering its effective water/powder ratio (0.33), and then functioned as wet ring lining materials. It is deduced that the effective water/powder ratio of the set specimen is lower than that of the original mix. The values with ceramic fibres were, however, not significantly different. Values similar to that for asbestos liner were obtained, meaning that ceramic fibres had the same effect on the accuracy of a metal crown as did the asbestos liner. In all cases except glass fibre (3T), the accuracy in using casting-ring liners was almost the same as the control measurement with asbestos liner.

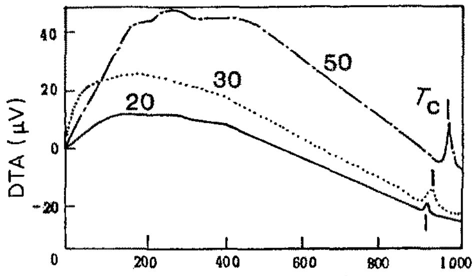

Figure 5 DTA curves for ceramic fibre (NEG). For key, see Fig. 3.

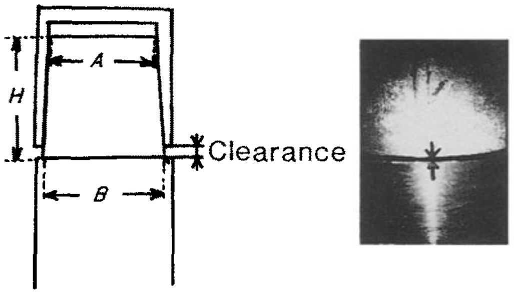

Figure 6 A schematic figure (cross-section) and optical micrograph for measuring the dimensional change. The clearance measured is indicated.

The largest value of the dimensional change shown in the measurement of glass fibre lining material (paper) as a ring liner suggests that the shrinkage of a metal crown tends to become smaller than the other ring liners would be desirable. Such new non-asbestos paper as glass fibre (twill) and ceramic fibre (NEG) could be applied as ring lining material.

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Received 20 June
and accepted 8 November 1989