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Thermoanalytical characteristics of powders in dental cast investment

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The present study examined the thermal properties of phosphate-bonded investments, a gypsum-bonded investment and an experimental investment powder when the basic powders were heated to high temperatures by simultaneous differential thermal analysis (DTA) and thermogravimetry (TG). The phosphate-bonded investments showed values of about 59 kcal mol^{-1} (247 kJ mol^{-1}) (thermal decomposition of $NH_4H_2PO_4$) and about 11 kcal mol^{-1} (46 kJ mol^{-1}) (formation of NH_4MgPO_4). Thermal reactions occurred clearly on the DTA–TG curves for the investment powders, using powders of $NH_4H_2PO_4$, and MgO with $NH_4H_2PO_4/MgO = 1$ as main components in the investment.

1. Introduction

Dental investment materials are used for the fabrication of small dental castings, depending on the melting range of the alloy. Gypsum-bonded materials are the older type for conventional gold alloys, while phosphate-bonded investments are designed primarily for higher-melting nickel- and cobalt-based alloys. It has been reported that when a cast phosphate-bonded specimen is heated, the formation of some compounds is observed in the range of test temperatures [1–7]. There have been several views on their formation: NH_4MgPO_4 which was formed during setting after mixing [1, 2], $Mg_2P_2O_7$, H_2O and NH_3 [1, 3–7] in the range of 200 to 300 °C, and $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$ at high temperatures [1, 3–7].

Thermal expansion is enhanced by the expansion of silica, such as cristobalite and quartz [1], and shrinkage is caused by the phosphate binder as in the thermal change of gypsum binder in gypsum-bonded investment [1, 8]. The powders showed a complicated thermal reaction because of the added water or special liquid. However, the thermal properties of the reaction products during heating in the absence of water or special liquid were little examined. In the present study, the activation energy for the reaction products was determined in the absence of mixing solution by means of simultaneous differential analysis (DTA) and thermogravimetry (TG). Additionally, the thermal reaction process was examined in an experimental phosphate-bonded investment compound for dental use.

2. Experimental procedure

Four commercial dental investments were tested: three phosphate-bonded investments of Ceravest (P1; GC Co, Tokyo), Sumavest (P2; Shofu Inc., Kyoto) and Crownvest (P3; Sankin Ind., Tokyo), and one gypsum-bonded cristobalite investment (CR; Shofu Inc., Kyoto). Two materials of $NH_4H_2PO_4$ (NHP; Wako Chem., Tokyo) and MgO (Nikato Co., Tokyo) were used for an experimental investment powder with $NH_4H_2PO_4/MgO = 1$.

Thermal reactions were done by heating to 900 °C at heating rates of 10, 30 and 50 °C min^{-1} in the thermal analysis equipment (DT-30; Shimadzu Co., Kyoto). The following thermal tests were performed: DTA and TG curves, activation energy for the formation of NH_4MgPO_4 and thermal decomposition of $NH_4H_2PO_4$, and heat during thermal decomposition. Thermal reactions in the range of test temperatures from room temperature to 900 °C were examined, and reaction products measured by X-ray diffraction patterns using CuK_α (X-ray diffraction equipment; Rigaku, Tokyo).

3. Results

Fig. 1 shows the X-ray intensity ratio of $NH_4H_2PO_4$ to MgO in each phosphate-bonded investment P1, P2 and P3, showing that the ratio ranged from 0.9 to 1.3. Figs 2 and 3 show thermoanalytical curves of DTA and TG. In Fig. 2a and b the curves of phosphate-bonded investment (P1) and gypsum-bonded cristobalite investment (CR) exhibit a peak temperature (T_p) representing thermal decomposition at about 200 °C, the temperature (T_m) of the formation of NH_4MgPO_4 at about 300 °C, and T_c and T_q (the transformation temperatures of cristobalite and quartz; 273 and 575 °C, respectively). In Fig. 3a and b the thermal changes of MgO and NHP, respectively, are shown. At the temperature T_0 thermal decomposition of NHP started and reached the peak temperature T_p. The MgO powder showed no thermal change, but NHP powder showed a weight loss with the progression of thermal decomposition.

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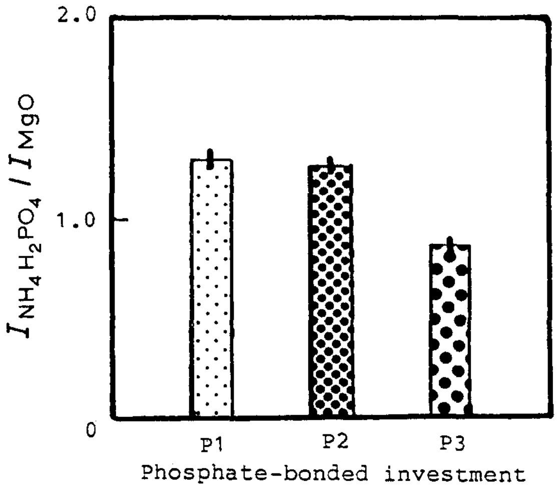

Figure 1 X-ray intensity ratio of $NH_4H_2PO_4$ to MgO in commercial phosphate-bonded investments P1, P2 and P3.

In Figs 4 and 5, the temperature T_p, the weight loss and the heat for thermal decomposition are shown for the materials tested. A heating-rate dependence of T_p and weight loss was observed for the investment and NHP powders tested. As a result the value of heat in NHP was larger than those in phosphate-bonded investments P1, P2 and P3, and nearly the same value as for $H_2O + NH_3$ was found for the phosphate-bonded investments. Using the experimental powder of NHP and MgO the results of Fig. 6 (DTA and TG curves) and Fig. 7a (X-ray diffraction lines of NHP and MgO) and 7b (X-ray diffraction line of NHP/MgO = 1) are given. On the basis of the results, thermal reactions (Table I) were deduced and the activation energies E_F (NH_4MgPO_4 formation) and E_D (thermal decomposition of $NH_4H_2PO_4$) for their reaction products were calculated by means of an Arrhenius plot [9]. Their values are shown in

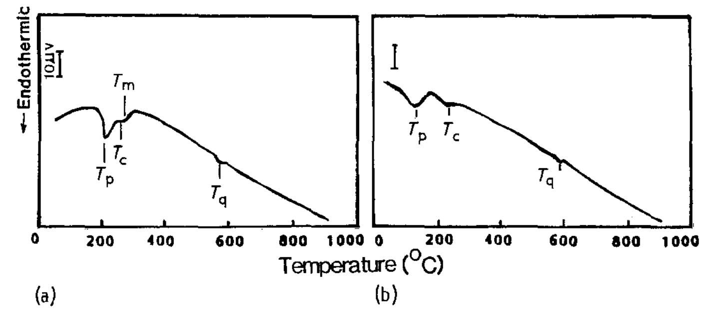

Figure 2 DTA curves for (a) phosphate-bonded investment P1 and (b) gypsum-bonded investment CR.

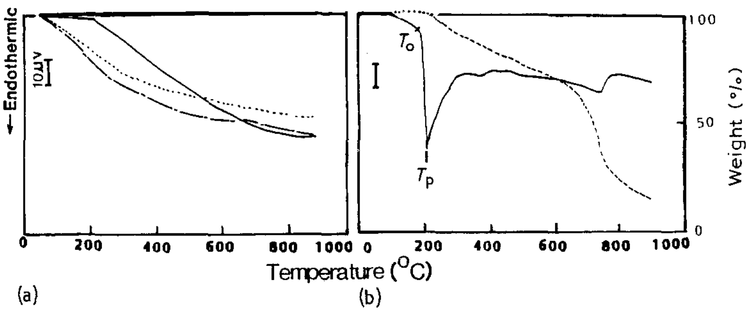

Figure 3 DTA and TG curves for (a) MgO powder and (b) $NH_4H_2PO_4$. Right-hand ordinate: (– – –) TGA. Left-hand ordinate: DTA at mean heating rate (. . .) 10, (—·—) 30 and (——) 50 °C min^{-1}.

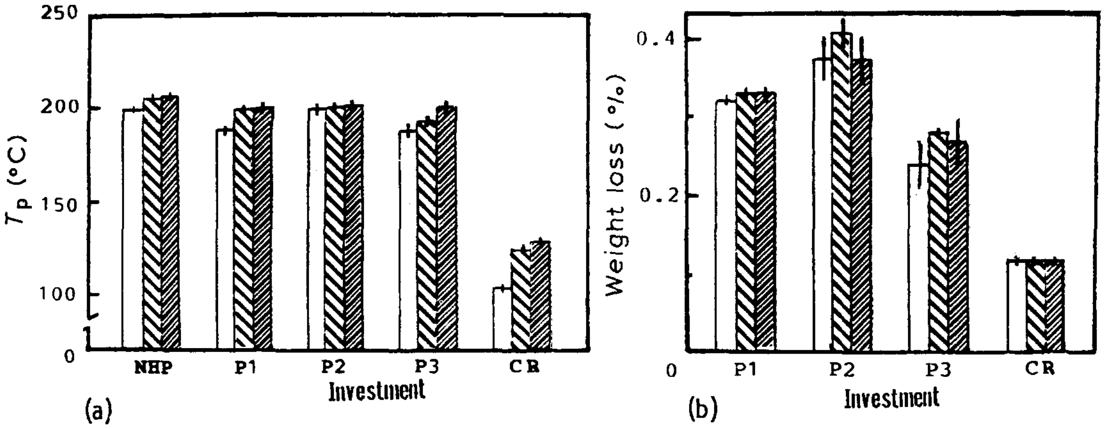

Figure 4 Thermal properties in materials tested at heating rate □ 10, ▧ 30 and ▨ 50 °C min^{-1}: (a) T_p temperature, (b) weight loss.

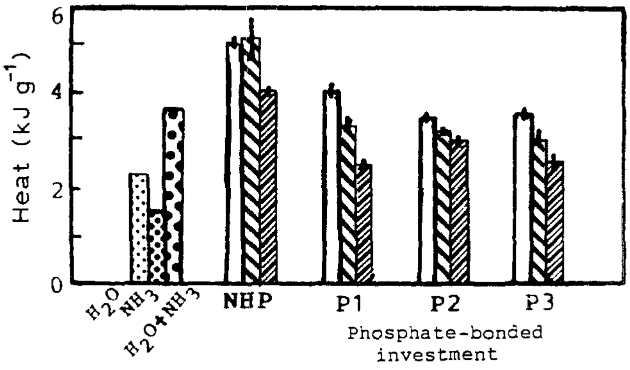

Figure 5 Heat during thermal decomposition in materials tested. For key, see Fig. 4.

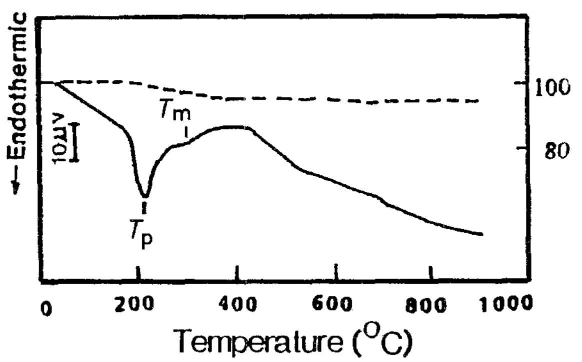

Figure 6 (——) DTA (left-hand ordinate) and (- - -) TG (right-hand ordinate) for experimental powders with NHP/MgO = 1.

Table II; the E_D values for P1–P3 were smaller than that of NHP powder.

4. Discussion

A ratio of $NH_4H_2PO_4$ to MgO powder of 1.0 was selected according to the result in Fig. 1 (change 0.9 to 1.3). Conventionally, the investment powder is mixed with water or a special liquid using a liquid/powder ratio of 0.15 to 0.35, and the setting reaction occurs during processing [1]. As setting appeared to be by reaction with liquid, the thermal analytical method was used for only the set investment. The setting reaction of phosphate-bonded investment started immediately after mixing it with the solution, and the temperature rose to above 60 °C within about 20 min [10]. As the resultant product was $NH_4MgPO_4 \cdot 6H_2O$, the hydration by H_2O would affect the thermal reaction during heating of the product. Therefore the thermal reaction due to investment itself would not be analysed.

TABLE I Thermal reactions as suggested from the results in the present study

At T_p:

$$nNH_4H_2PO_4 \rightarrow nH_3PO_4 + nNH_3\uparrow$$

$$nNH_4H_2PO_4 \rightarrow (NH_4PO_3)_n + nH_2O\uparrow$$

At T_m:

$$(NH_4PO_3)_n + nMgO \rightarrow (NH_4MgPO_4)_n$$

$T \geqslant T_m$:

$$2(NH_4MgPO_4)_n \rightarrow (Mg_2P_2O_7)_n + 2nNH_3\uparrow + nH_2O\uparrow$$

TABLE II Values of activation energy E_D and E_F in the materials investigated (E_D = thermal decomposition of $NH_4H_2PO_4$, E_F = formation of NH_4MgPO_4)

Material	Activation energy (kcal mol^{-1})^a	
	E_D	E_F
P1	62.4	10.9
P2	56.0	13.3
P3	58.4	10.0
NHP	72.0	–

^{a} 1 kcal mol^{-1} = 4.187 kJ mol^{-1}.

In the present study the DTA–TG results obtained are in Figs. 2 to 6, and summarized in Table II. In commercial phosphate-bonded investments one endothermic peak, corresponding to thermal decomposition of $NH_4H_2PO_4$, appeared at about 200 °C (Fig. 4a). One exothermic start temperature T_m appeared at about 300 °C. In the investments including cristobalite and quartz the α–β transformation temperatures were observed as T_c and T_q temperatures.

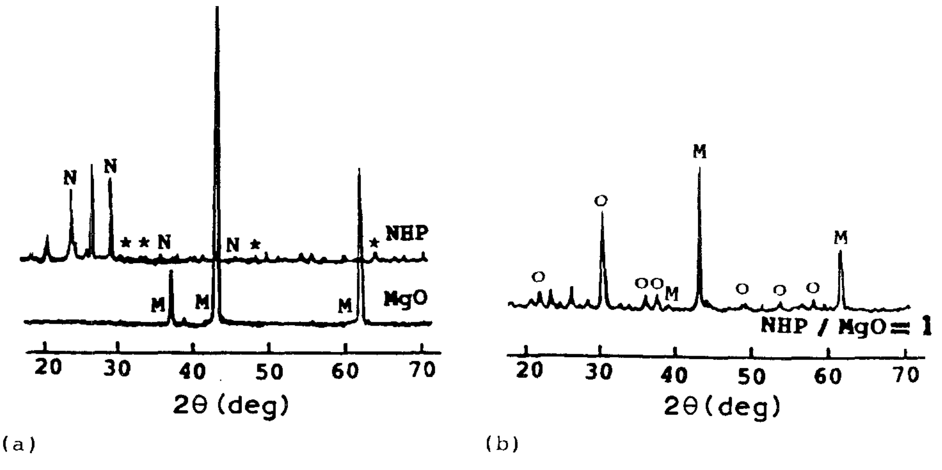

Figure 7 X-ray diffraction lines for (a) NHP and MgO (as-received) and (b) NHP/MgO = 1 (heated at 900 °C for 1 h). (N) $NH_4H_2PO_4$, (★) $(NH_4PO_3)_n$, (M) MgO, (O) $Mg_2P_2O_7$.

As shown in Fig. 4, the thermal decomposition temperature (T_p) in phosphate-bonded investments occurred by the decomposition of NHP. In the case of gypsum-bonded investment (CR) used without water the dehydration of calcium sulphate dihydride to anhydride appeared at a lower temperature of about 110 to 130 °C, compared with the endothermic peak temperature at about 200 °C of the set investment mixed with water as reported elsewhere [1, 11].

Because the complicated DTA curve includes dehydration and vaporization of the water used for mixing, the curve was not plotted for the set investment. However, such thermal properties as the peak temperature and activation energy for thermal decomposition were clearly determined here. The thermal decomposition at T_p in phosphate-bonded investments could occur with the occurrence of H_2O and NH_3 as shown by the values in Fig. 5. The activation energy for the decomposition ranged from 56.0 to 62.4 kcal mol^{-1} (234 to 261 kJ mol^{-1}), showing lower values than the NHP powder (72.0 kcal mol^{-1} or 301 kJ mol^{-1}). As indicated in Table I, the oxide compound of NH_4MgPO_4 formed at almost the same value (about 11.4 kcal mol^{-1} or 47.7 kJ mol^{-1}). Thus, these results indicate that the investment could make NH_4MgPO_4 easily at a low activation energy by including MgO in the investment powders. The appropriate amount of MgO in the investment was not, however, determined in this study. Following this formation the oxide $Mg_2P_2O_7$ could be made at higher test temperatures in the thermal reactions indicated in Table I.

The thermal change of the materials tested was examined in relation to the formation and thermal decomposition occurring in raising the test temperature. It appears that the thermal reaction due to the decomposition of $NH_4H_2PO_4$ nearly equals the energy of heat due to the occurrence of H_2O and NH_3. The formation of NH_4MgPO_4 is influenced by the MgO powder in phosphate-bonded investments after thermal decomposition at higher test temperatures. These results could lead to the development of new phosphate-bonded investments for dental application.

References

1. R. W. PHILLIPS, "Skinner's Science of Dental Materials", 8th Edn (Saunders, Philadelphia, 1982) p. 408.
2. R. J. SCHNELL, G. MUNFORD and R. W. PHILLIPS, *J. Prosthet. Dent.* **13** (1963) 324.
3. D. W. JONES, *ibid.* **18** (1967) 234.
4. M. WATANABE, *Shizaiki-shi* **18** (1968) 12.
5. *Idem Koukuu byou-shi* **36** (1969) 147.
6. *Idem, ibid.* **36** (1969) 122.
7. W. FINGER and K. KOTA, *Scand. J. Dent. Res.* **90** (1982) 243.
8. T. MORI, *J. Dent. Res.* **64** (1985) 658.
9. K. WAKASA and M. YAMAKI, *J. Mater. Sci.* **23** (1988) 1459.
10. F. A. MARSAW, W. G. de RIJK, R. A. HESBY, R. W. HINMAN and G. B. PELLEU, *J. Prosthet. Dent.* **52** (1984) 361.
11. T. MORI, *J. Dent. Res.* **65** (1986) 877.

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