The strengthening mechanism of a magnesia core ceramic

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Abstract. A high-expansion core material containing magnesia and forsterite may be used to make all-ceramic dental crowns with porcelain-fused-to-metal body porcelains. The purpose of this study was to investigate the strengthening mechanism for the magnesia core material. Six batches of the magnesia core material were made by reacting magnesia with a silica glass with holding times ranging from 17 to 120 min. The flexural strength was measured using three-point loading according to the ISO specification for dental ceramics. The forsterite content was measured using quantitative x-ray diffraction. A statistically significant correlation was found between the forsterite content and flexural strength. The proposed mechanism for strengthening is the precipitation of fine forsterite crystals in the glass matrix surrounding unreacted magnesia. Longer reaction times produced more dissolution of magnesia and subsequent precipitation of forsterite. This method results in a new strengthening mechanism for dental ceramics which have previously relied on the incorporation of alumina, leucite or ceramic whiskers.

INTRODUCTION

Porcelain jacket crowns have been used in dentistry since 1903. However, the low strengths of these materials precluded their widespread use. In 1965, the alumina-reinforced porcelain crown was introduced. A typical alumina-reinforced porcelain has a flexural strength of approximately 131 MPa, twice that of feldspathic porcelains. Other methods of reinforcing dental porcelains have since been developed.

Methods for determining the flexural strength of dental porcelains have been described by Jones et al. (1972) and Edwards et al. (1983). McLean and Hughes (1965), McLean (1967), McLean and Kedge (1987), and Seghi et al. (1990) have reported on the flexural strengths of various reinforced porcelains.
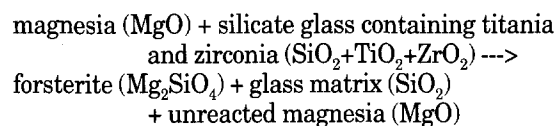
Magnesia is the basis of an experimental high expansion ceramic core material for the construction of all-ceramic dental crowns (O'Brien, 1985). Since the coefficient of thermal expansion of this core material has an average coefficient of expansion of $14.5 \times 10^{-6}/°C$ (23°C - 500°C), it can be used with body and incisal porcelains designed for bonding to metals (e.g., Ceramco II, Ceramco Inc., Burlington, NJ, USA; Vita VWK 68, Vident Inc., Baldwin Park, CA, USA; Crystar, Unitek Corp., Morovia, CA, USA; Will-Ceram, Williams Dental, Amherst, NJ, USA; Excelco

Porcelain, Excelco International, Deerfield Beach, FL, USA; etc.) to construct reinforced porcelain jacket crowns. This is not possible with aluminous core materials since they have coefficients of expansion around $8.0 \times 10^{-6}/°C$ and the porcelain-fused-to-metal porcelains have values around $13.5 \times 10^{-6}/°C$. Flexural strength values for the magnesia core porcelain have been reported by O'Brien et al. (1988) and Hondrum and O'Brien (1988) to be 131 MPa.

The purpose of this study was to investigate the strengthening mechanism for the magnesia core material. The hypothesis was that forsterite crystallization during the synthesis contributes to the strength as well as residual unreacted magnesia (O'Brien and O'Brien, 1986).

MATERIALS AND METHODS

Six batches of the magnesia core material were made by reacting 40% by weight of magnesia with 60% of a silica glass with the composition given in Table 1. The temperature as a function of time was monitored using a platinum/platinum-rhodium (10%) thermocouple and recorded (Model 660, Thermocouple Thermometer, Omega Engineering Inc., Stamford, CT, USA). The holding times at 1100-1150°C ranged between 17 to 120 min to form different quantities of forsterite (Mg_2SiO_4) by the reaction:

magnesia (MgO) + silicate glass containing titania
and zirconia ($SiO_2+TiO_2+ZrO_2$) --->
forsterite (Mg_2SiO_4) + glass matrix (SiO_2)
+ unreacted magnesia (MgO)

The frits were quenched in water and dried overnight. The materials were then pulverized with a mortar and pestle, ground (Model 155, Mortar Grinder, Fisher Scientific, Pittsburgh, PA, USA) and sieved (Model L3P, Sonic Sifter, Allen Bradley, Milwaukee, WI, USA) to obtain a fine powder. A series of sieves with openings of 2 mm, 500 µm, 105 µm, 74 µm, 63 µm, 53 µm, and 37 µm were used to screen the powder.

The forsterite content of the magnesia core porcelains produced by different holding times was determined using quantitative x-ray diffraction with silicon as the internal standard. In this method, a diffraction line from the phase being determined is compared with a line from a standard substance mixed with the sample in known proportions (Cullity, 1978). Four calibration standards were prepared with synthetic forsterite (Mason Colors,

TABLE 1: COMPOSITION OF GLASS USED IN THE SYNTHESIS OF THE MAGNESIA CORE MATERIAL

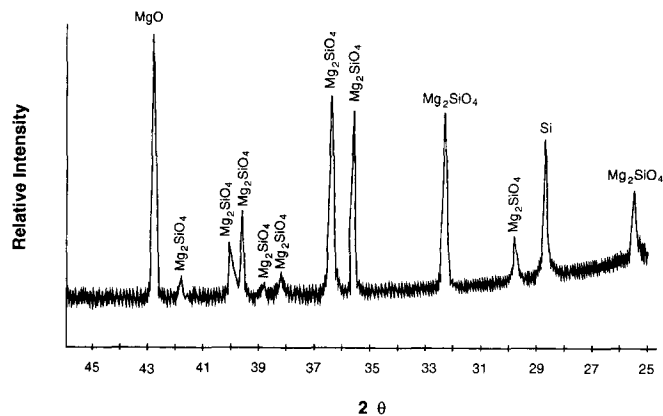| Compound	Weight Percent
SiO_2	58.0
Al_2O_3	1.5
TiO_2	5.0
ZrO_2	6.0
Na_2O	10.0
K_2O	5.0
B_2O_3	9.5
F	5.0

Fig. 1. An x-ray diffraction pattern of the magnesia ceramic with the silicon standard.
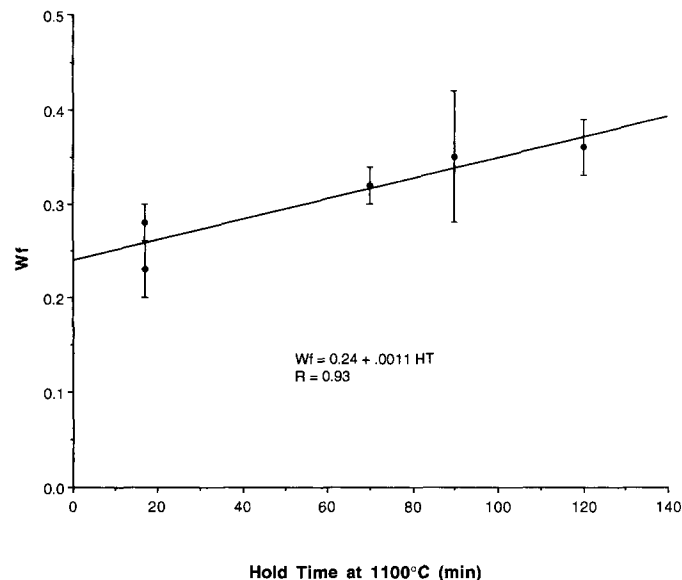

Fig. 2. The calibration curve generated by plotting the ratio of the peak intensities (I_f/I_s) as a function of the weight fraction of forsterite (W_f).
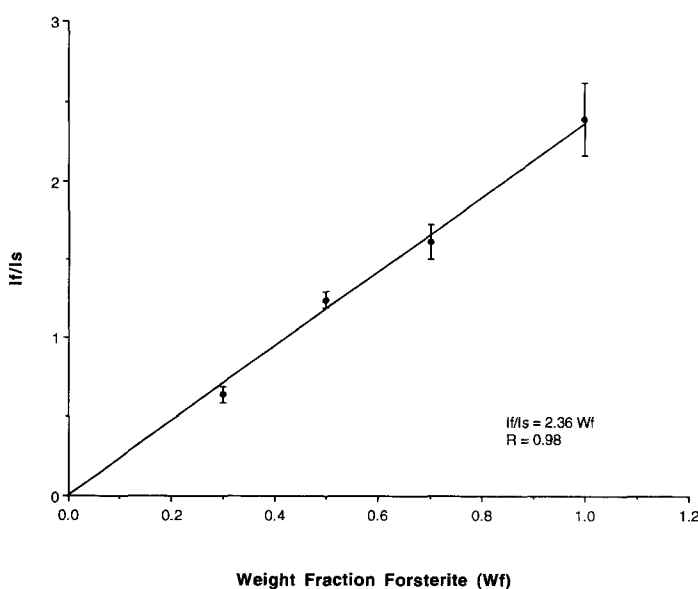

Fig. 3. The weight fraction of forsterite in the magnesia core material as a function of the holding time at 1100°C.

East Liverpool, OH, USA) and the silica glass given in Table 1. The levels of forsterite in these standards were 30, 50, 70 and 100 wt%, and the balance was the silica glass from Table 1. Eighteen parts of each standard were mixed with one part of silicon (Stock No. S-1053, Cerac Inc., Milwaukee, WI, USA) prior to x-ray analysis. Six x-ray diffraction patterns were recorded over the 2Θ range of 25-35° for each of the standards using an x-ray diffractometer (Model XRG-3000, Philips Electronic Instruments, Mount Vernon, NY, USA). In this 2Θ range, the forsterite peak at 32.4° (d = 0.277 nm) and a silicon peak at 28.7° (d = 0.314 nm) were suitable for quantitative analysis (Fig. 1). The calibration curve (Fig. 2) was the linear regression passing through the origin of the ratio of the peak intensities (I_f/I_s) as a function of the weight fraction of forsterite (W_f).

The forsterite contents of the six experimental batches were determined using the calibration curve generated above. Eighteen parts of the <37 µm particle size fraction of each batch were mixed with one part of silicon prior to x-ray analysis. Six x-ray diffraction patterns were recorded over the 2Θ range of 25-35° for each of the batches. The ratio of the peak intensities $(I_f$ at 32.4°/I_s at 28.7°) was plotted on the calibration curve, and the weight fraction of forsterite (W_f) was determined.

The bars for determination of flexural strength were fired at 1120°C with a 5 min hold (Cera-Mat III, Jelrus Technical Products Corp., New Hyde Park, NY, USA) for each of the six batches. The flexural strength was measured on a minimum of six 20x5x1.75 mm specimens per batch using three-point loading and following the ISO Specification 6872 (1984) for dental ceramics with a tension and compression tester (Model HTC, John Chatillon & Sons, New York, NY, USA). A feldspathic porcelain and a reinforced porcelain (Brush Opaque, Excelco International; and Optec HSP, Jeneric/Pentron, Wallingford, CT, USA) served as controls. The results were analyzed by an ANOVA and Scheffé multiple comparisons test.

RESULTS

A summary of the synthesis, x-ray diffraction, and flexural strength results is provided in Table 2.

There is a high correlation (R=0.93, p=0.022) between the weight fraction of forsterite formed and the holding times at 1100°C. This is illustrated in Fig. 3.

Fig. 1 shows a diffraction pattern from the magnesia ceramic with the silicon standard. Analysis of the pattern showed the presence of MgO, Si standard, and forsterite (Mg_2SiO_4). The

TABLE 2: A SUMMARY OF THE RESULTS OF SIX BATCHES OF MAGNESIA CORE MATERIAL			
Batch	Hold Time at 1100°C (min)	Weight Fraction of Forsterite (W_f) Mean (SD)	Flexural Strength (MPa) Mean (SD)
51190	17	0.23 (0.03)	104 (13)
51790	17	0.28 (0.02)	120 (6)
70990	70	0.32 (0.02)	122 (19)
91890	120	0.36 (0.03)	130 (13)
121990		0.42 (0.03)	140 (12)
70291	90	0.35 (0.07)	145 (9)
Groups joined by vertical lines are not significantly different ($p < 0.05$).			

Fig. 4. The flexural strengths of the magnesia core material plotted against the mean weight fraction of forsterite.

calibration curve for the forsterite, shown in Fig. 2, shows a high correlation ($R = 0.98$, $p < 0.0001$) between the ratio of the peak intensities (I_f/I_s) and the weight fraction of forsterite (W_f).

The flexural strengths of the magnesia core material fritted for different times plotted against the mean weight fraction of forsterite is given in Fig. 4. The weight fraction of forsterite formed ranged from 0.23 to 0.42, and the flexural strength values ranged from 104 to 145 MPa. An ANOVA and Scheffé test showed that there was a significant effect of batch on the flexural strength ($p < 0.0001$). Batch one was significantly weaker than batches four, five, and six, while batch six was significantly stronger than batches one and two (Table 2). Linear regression revealed a significant correlation ($R = 0.88$, $p = 0.022$) between the mean forsterite contents and the mean flexural strengths. The average strength of the component glass (Table 1) was 51 MPa. Extrapolation of the linear regression line to zero forsterite content gave a strength value of 63 MPa. Results from previous studies (O'Brien et al., 1988; Hondrum and O'Brien, 1988) are within the range reported here. The feldspathic porcelain and the reinforced porcelain had flexural strengths of 101±8 MPa and 152±8 MPa, respectively.

DISCUSSION

The internal standard method is valid only for integrated intensities. The peak height method of simply measuring maximum intensities is permissible when the shape of the diffraction lines is found to be essentially constant from sample to sample. As long as all patterns are made under identical experimental conditions, there is a constant proportionality between maximum and integrated intensities, and the measurement of maximum intensities gives satisfactory results (Cullity, 1978).

The correlation between flexural strength and forsterite content supported the hypothesis that the magnesia core material was strengthened by the dispersion of fine crystalline silicates in a glassy matrix (see Fig. 5) and indicated that forsterite makes a major contribution to the strength of the magnesia ceramic. Fig. 5 shows the microstructure of the fired magnesia ceramic which was prepared and finished to a 1 μm diamond polish using standard metallographic procedures. A microprobe analysis showed the presence of unreacted magnesia and an amphorous matrix containing a fine precipitate of forsterite, smaller amounts of enstatite and minor amounts of magnesium zirconium silicate and magnesium titanium silicate compounds. The titanium dioxide and zironium oxides in the glass (Table 1) used to form the
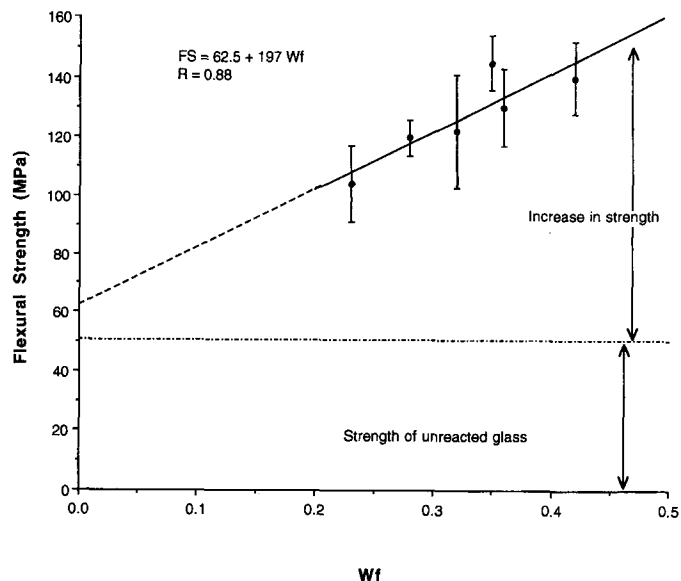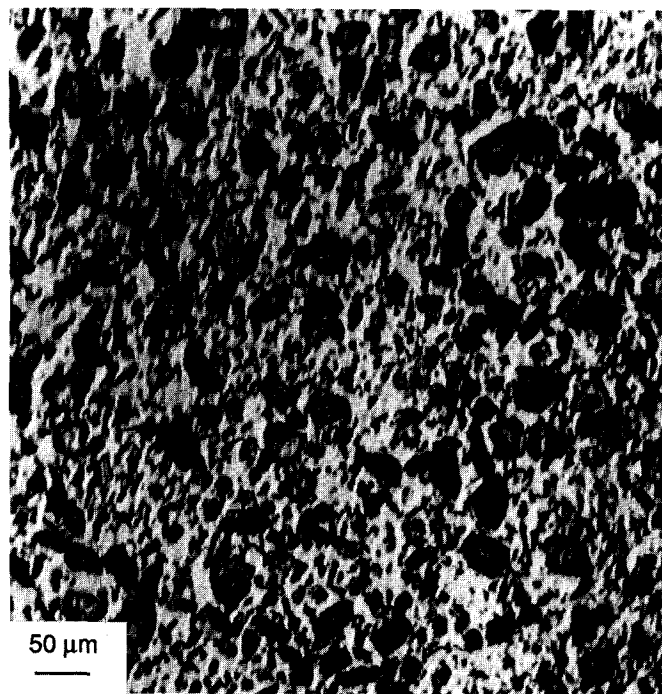

Fig. 5. The microstructure of the fired magnesia ceramic showing magnesia and reaction products dispersed in the matrix.

magnesia ceramic are known to be nucleating agents in glass crystallization (McMillan, 1979) and may contribute to the formation of forsterite and enstatite. The presence of minor amounts of magnesium zirconium silicates and magnesium titanium silicates may also contribute to the strengthening of the magnesia core material.

The proposed mechanism for strengthening is the precipitation of fine forsterite crystals in the glass matrix surrounding unreacted magnesia. Longer reaction times produced more dissolution of magnesia and subsequent precipitation of forsterite. This method results in a new strengthening mechanism for dental ceramics which have previously relied on the incorporation of leucite or alumina.

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