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THERMAL ANALYSES OF THE DENTAL GLASS–CERAMIC DICOR IN REGARD TO THE DEVELOPMENT OF A TWO–LAYERED TEXTURE

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SUMMARY

The crystallization process of the dental glass–ceramic Dicor is investigated by DSC and the texture is shown by electron microscopy. Dilatometric measurements demonstrate the conformity of the thermal expansion of the glass and the special investment, which is used for embedding the glassy blank during crystallization.

INTRODUCTION

Increasing demands on the esthetics of fixed bridges and the desire for improvements in dental technology have led to the development of the glass–ceramic Dicor (DeTrey/Dentsply, Dreieich, FRG), used as a bioinert material for crowns, inlays, and bridges.

The manufactering process starts with the casting of a machinable glassy blank by applying the lost wax method. The crystallization ('ceramization') of the glass is carried out in a special furnace by heating with a rate of 10 °C/min up to 1075 °C, holding the temperature for 6 hours and cooling again with a rate of 10 °C/min down to at least 500 °C (ref. 1). During this procedure the glass is embedded in a special investment consisting of leucite ($K[AlSi_2O_6]$) and gypsum ($CaSO_4 \cdot 2H_2O$) (ref. 2).

The texture of the glass–ceramic is based on the crystallization of the tetrasilicic mica $K_2Mg_5[F_4|Si_8O_{20}]$ in a glass of the quaternary system K_2O–MgF_2–MgO–SiO_2 (ref. 3). Due to an ion exchange with the ceramization investment the superficial layer of the glass–ceramic shows a loss of K^+ and a gain of Ca^{2+} (ref. 2) and in addition a loss of F^- (ref. 4), thus the chemical composition in this area is changed to a MgO–SiO_2 system where enstatite ($Mg_2[Si_2O_6]$) is stable (ref. 2).

The thermal analysis of the crystallization process as well as the thermal compatibility of ceramization investment and glass are investigated in this study.

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METHODS

DSC measurements (computer controlled Netzsch DTA 404 S) were performed to determine the crystallization temperature of mica in the glass. In regard to the loss of F^- at the surface during heating a bulk sample was used, which completely filled up the Al_2O_3 crucible. The thermal expansion of glass and ceramization investment was determined by dilatometry (Netzsch TMA 402 E). In all measurements the heating rate was 5 °C/min in consideration of usual practice; accuracy of temperature measurements is within ±5 °C. The texture of the glass–ceramic was investigated by electron microscopy after etching with 5% HF for 3 min.

RESULTS

The DSC measurement of the glass sample is shown in Fig. 1. An exothermal reaction between 667 °C and 689 °C indicates the crystallization of mica while the endothermal reaction between 1157 °C and 1188 °C represents the dissolution of the crystalline mica phase.

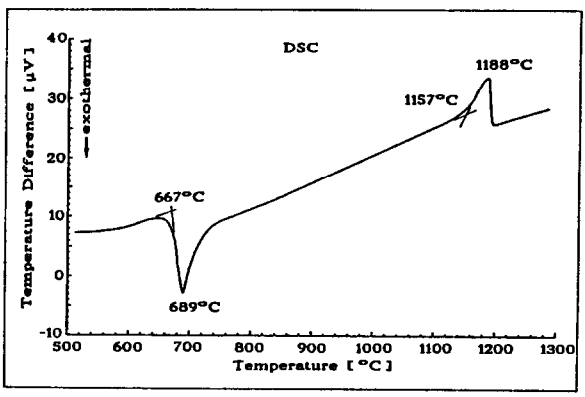

Fig. 1: DSC of the glass; heating rate 5 °C/min.

Etching of the samples reveals the crystalline phases. Fig. 2 (left) shows typical crystallites of mica with sizes ranging from 0.5 to 2 µm in diameter. This texture exists in the whole glass–ceramic except near the surface, where down to a depth of about 50–80 µm palisade like prismatic enstatite appears as a result of the ion exchange described above (Fig. 2 right).

The linear thermal expansion of the ceramization investment is mainly influenced by the reaction of leucite, the main component of the investment (Fig. 3). The second order phase transition of leucite causes an increase of the thermal expansion up to 675 °C. In this region the cubic structure is stable and only little more thermal expansion occurs.

In the investment the phase transitions of gypsum partly counteract the thermal expansion of leucite. Both the loss of H_2O at 130 °C and the phase transition of $CaSO_4$ at 370 °C result in a considerable volume reduction. Above 470 °C the curve resembles to that of leucite, reaching a plateau at 670 °C and being stable until decomposition of $CaSO_4$ takes place.

The thermal expansion of the glass is very low ($\alpha_{25-600\ °C} = 1.13 \cdot 10^{-6}/°C$). The transformation point (T_g) is at 612 °C and the softening point at 655 °C. Fig. 1 shows that the cystallization beginns at 667 °C. This procedure leads to a more rigid glass–ceramic, demonstrated by the flattening of the dilatometric curve at 900 °C. At 950 °C the softening point of the glass–ceramic is reached.

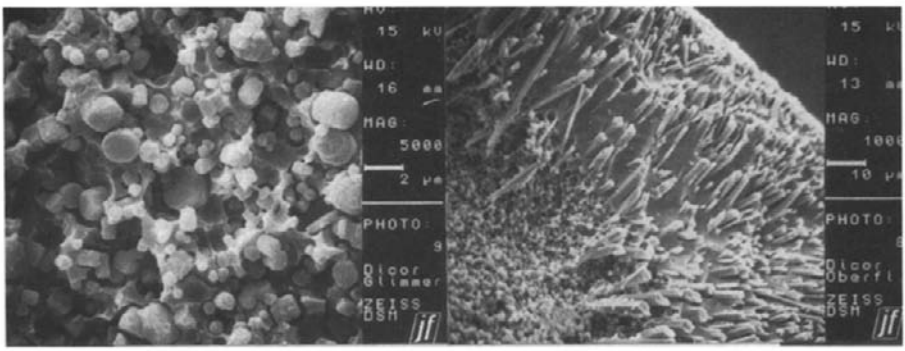

Fig. 2: Electron microscopy view of the glass–ceramic;
left: mica crystallites, right: enstatite layer.

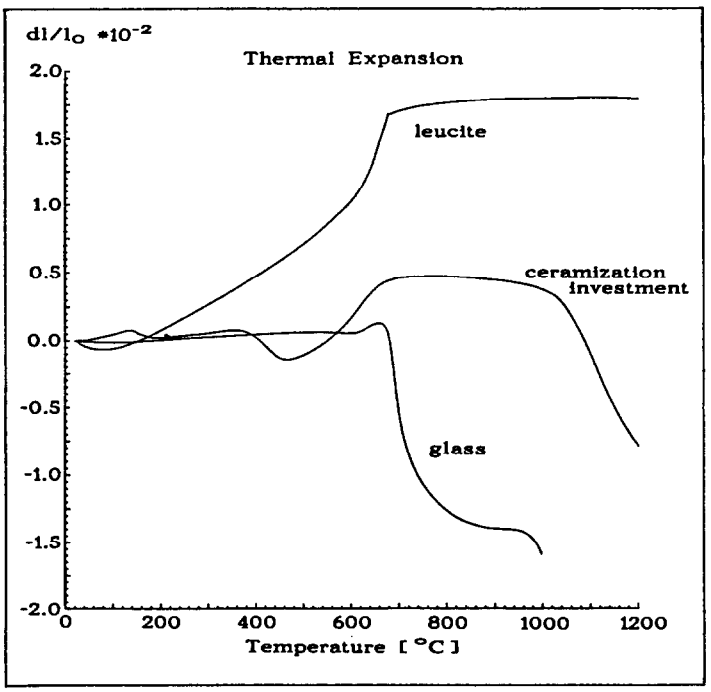

Fig. 3: Dilatometric measurements of leucite, investment, and glass;
heating rate 5 ^{0}C/min.

Comparing the thermal expansions of ceramization investment and glass it is obvious that up to the transformation range of the glass the expansions of both fit very well together. The slight expansion of the glass above T_g is accompanied by the expansion of the investment caused by leucite. During softening and crystallization of the glass the investment stabilizes the form of the embedded piece until the crystallization is advanced and the glass reacts more rigid. Above 1000 ^{0}C the decomposition of $CaSO_4$ enables the ion exchange, which is carried out at 1075 ^{0}C.

DISCUSSION

The results demonstrate, that the ceramization process of the dental glass–ceramic Dicor is a thermally well harmonized system. Due to its composition the investment shows a low thermal expansion almost similar to that of the glass. There will be no crack formation in the investment, which would disturb the ion exchange and cause deformations of the embedded piece. A comparison of the DSC and the dilatometric curves of the glass reveals, that the crystallization process is not finished at 689 ^{0}C, as the DSC might be interpreted. Because the dilatometric curve is reaching a plateau at about 900 ^{0}C in spite of the increasing temperature, a continual reduction of the glassy phase up to this temperature can be deduced. During the crystallization of the glass between 667 ^{0}C and about 900 ^{0}C the constant volume of the investment ensures that no deformation of the embedded piece can occur.

The formation of the enstatite containing layer resembles to the arrangement of the natural prismatic enamel. Thus the practical meaning of the enstatite layer is to be seen in an optical effect, which pretends the appearance of natural teeth.

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