PHASE FORMATION AND PROPERTIES OF DENTAL GLASS-CERAMICS IN THE SiO_2 - Al_2O_3 - K_2O - CaO - P_2O_5 AND SiO_2 - Li_2O - ZrO_2 - P_2O_5 SYSTEMS

WOLFRAM HÖLAND

Ivoclar Ltd., FL - 9494 Schaan, Principality of Liechtenstein

Abstract Two glass-ceramics were used to demonstrate that P_2O_5 has different effects on the controlled crystallization of glasses. In the first system, P_2O_5 promoted the formation of needle-like apatite. In the second system, P_2O_5 improved the formation of glasses with a high ZrO_2 content. The controlling of crystallization permitted the formation of ZrO_2 - and Li_3PO_4 -crystals.

INTRODUCTION

The different effects of the phosphate on the two glass-ceramics were studied with the objective of developing glass-ceramics from base glass powders by controlled sintering, nucleation, and crystallization. The aim was to develop leucite, KAlSi_2O_6 and a special needle-like apatite on the one hand and a high ZrO_2 -crystal content of the glass-ceramics on the other.

Abe et al. [1] produced anisotropically grown chain phosphates in glass-ceramics. The formation of needle-like apatite crystals was achieved only under hydrothermal conditions [2] and not from the glass melt. These crystals are similar to those found in natural teeth for example.

Glass-ceramics containing ZrO_2 were developed in various silicate glass-ceramic systems with contents of approx. 10 wt% [3-5]. The objective of this study was to incorporate a great deal more than 10 wt% ZrO_2 in glass-ceramics and thus achieve new conditions for controlled crystallization. The addition of P_2O_5 was effective.

EXPERIMENTAL PROCEDURE

Both types of glass-ceramics were produced as sintered glass-ceramics from powdered base glasses. For the first type of glass-ceramic system, small amounts of

FIGURE 1. Number and length of needle-like apatite as a function of time for apatite leucite glass-ceramic at 1050 °C.

0.5 - 6 wt% P_2O_5 were incorporated into glasses of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-CaO}$ system. Additives of P_2O_5 allow both leucite and apatite crystal precipitation to be controlled [6]. The final biomaterial was prepared by sintering.

In the second type of material, 10 wt% P_2O_5 were incorporated into glasses of the $\text{SiO}_2\text{-Li}_2\text{O-ZrO}_2$ system. The influence of controlled crystallization on the formation of crystals with a high ZrO_2 content was examined by heat treating the glasses. Hence, a monolithic raw glass-ceramic was formed into a glass-ceramic ingot by sintering the powdered base glass. Subsequently, the ingot underwent a "viscous flow" process at 1000 °C, low pressure of 0.5 MPa and viscosity of $10^5\text{-}10^6$ Pa·s to produce a biomaterial.

FIGURE 2. Microstructure of needle-like apatite leucite glass-ceramic with heat treatment at 1050 °C/20 min. SEM.

FIGURE 3. ZrO_2 and Li_3PO_4 crystals formed after pressing at 1000 °C. SEM.

RESULTS AND DISCUSSION

Glasses in the composition range of 49 - 58 wt% SiO₂, 11 - 19 Al₂O₃, 9 - 23 K₂O, 1 - 10 Na₂O, 2 - 12 CaO, 0.5 - 6 P₂O₅, 1 - 9 ZrO₂, 0.2 - 2.5 F (with additives of up to 6 wt% being possible and preferably CeO₂, B₂O₃, Li₂O) permit controlled crystallization of leucite and needle-like apatite. A CaO/P₂O₅ molar ratio of approx. 5.8 and a fluorine content of 0.6 wt% of the base glass was preferred. Leucite was formed according to surface nucleation mechanisms on the inner "ghost" surfaces of the powdered glass. The leucite content was approx. 10 - 25 vol%. The formation of apatite proceeded according to the mechanism of bulk nucleation. The apatite content was approx. 5 - 10 vol%. Phase separation in the base glass represents the beginning of nucleation in the apatite formation mechanism. Base glasses showed that this stage of nucleation, however, proceeded very quickly. As a result, a large number of small needle-like apatite crystals was present when the glass had only been heat treated for a short time (10 min) at 1050 °C. Figures 1 and 2 demonstrate that during longer heat treatments, the number of the crystallites decreased, and the crystals grew in a needle-like, anisotropic manner to a size of approx. 5 µm. These results showed that the growth process of needle-like apatites proceeded according to the mechanism of Ostwald ripening. This means that the solid state reactions would have to be characterized by high ion mobility and diffusion.

In the second glass-ceramic system, the effect of P₂O₅ was demonstrated in another manner [10]. This glass was in the range of 42 - 59 wt% SiO₂, 7 - 15 Li₂O, 4 - 14 P₂O₅, 15 - 28 ZrO₂. Furthermore, approx. 11 wt% K₂O, Na₂O, Al₂O₃ and F were also added. The addition of preferably 10 wt% P₂O₅, to base glasses of the SiO₂ - Li₂O - ZrO₂ system with preferably 20 wt% ZrO₂ permitted an increase in the glass forming tendency. The crystal formation process was characterized by two mechanisms: Surface nucleation of ZrSiO₄ crystals and bulk nucleation of ZrO₂- and Li₃PO₄-type crystals. The main crystal phases underwent a specific growth process. Li₃PO₄ crystals developed within the spherical droplet glass phase during primary crystallization and grew with heat treatment, e.g. at 950 °C/10 hours, into rod-shaped crystals. ZrO₂ crystals of the baddeleyite-type and the tetragonal modification were also formed into crystallites of 200 - 300 nm after primary crystallization at 940 °C/4 hours and grew into needle-like crystals of 1 - 20 µm in length at 1000 °C/6 hours. The crystal content, as well as the size of the two phases influenced the mechanical parameters of the glass-ceramics. The microstructure of the glass-ceramic material was optimized according to these findings. Hence, having undergone the "viscous pressing" procedure at 1000°C, the glass-ceramic material featured the microstructure shown in Fig 3. Furthermore, it

demonstrates strength of approx. 280 MPa and fracture toughness, as K_{IC} of $2.0\text{MPa}\cdot\text{m}^{0.5}$.

SUMMARY

When sintered, the apatite-leucite glass-ceramic can be used as dental material as a veneering material for metal substrates, e.g. dental bridges. The glass-ceramic material is translucent and its coefficient of thermal expansion can be adjusted between 12 and $16 \cdot 10^{-6}\text{K}^{-1}\text{m/m}$. The ZrO_2 glass-ceramic material can also be used for dental applications. The material is joined to ZrO_2 posts to produce biocompatible restorations.

ACKNOWLEDGEMENTS

The author wishes to thank his co-workers M. Frank, M. Schweiger, S. Wegner, V. Rheinberger for their contribution to this comprehensive multi-disciplinary investigation.

REFERENCES

- 1 Y. Abe, T. Kasuga, H. Hosono and K. de Groot, J. Amer. Ceram. Soc., **67**, C142 (1984).
- 2 H. Newesely, Mechanism and action of trace elements in the mineralisation of dental hard tissues, Zyma SA (1972)
- 3 T. Uno, T. Kasuga, S. Takayamana, A.J. Ikushima, J. Amer. Ceram. Soc., **76**, 539 (1993).
- 4 L.M. Echeverria and G.H. Beall, Ceram. Trans., **22**, 235 (1991).
- 5 M.I. Budd, J. Mat. Sci., **28**, 1007 (1993).
- 6 W. Höland, M. Frank, M. Schweiger and V. Rheinberger, Glastechn. Ber. Glass Sci. Technol. **67 C**, 117 (1994).
- 7 W. Höland, M. Frank, M. Schweiger, S. Wegner, V. Rheinberger, Glastech. Ber. Glass Sci. Technol., **69**, 1 (1996).