



Phase and microstructure formation and their influence on the strength of two types of glass-ceramics



M. Dittmer^{a,*}, C. Ritzberger^a, M. Schweiger^a, V. Rheinberger^a, M. Wörle^b, W. Höland^a

^a Ivoclar Vivadent AG, Bendererstr. 2, 9494 Schaan, Principality of Liechtenstein

^b ETH Zurich, Wolfgang-Pauli-Str. 10, 8093 Zurich, Switzerland

ARTICLE INFO

Article history:

Received 30 November 2012

Received in revised form 12 February 2013

Available online 2 April 2013

Keywords:

Glass-ceramics;

Microstructure formation;

Crystal content;

Flexural strength

ABSTRACT

The aim of this publication is to examine the phase and the microstructure formation of two different glass-ceramic systems. While the formation of crystal phases with a high coefficient of thermal expansion (low-quartz and spinel) is responsible for imparting strengths of up to 475 MPa to the magnesium aluminosilicate system, a dense crystal microstructure provides the strength in the lithium silicate system. Therefore, the second part of this publication describes a method which allows initial conclusions to be drawn regarding the achievable strength values. For this purpose, the crystal phase content of powders was studied on the basis of scanning electron micrograph pictures and by means of Rietveld refinement analysis, using Al_2O_3 as the internal standard. On the scanning electron micrographs, the crystal phase content was established by determining the “relative crystal areas” of the different specimens and subsequently evaluating them using a program called “Analysis”. This allowed the attainable strength values to be predicted. In this evaluation, composition C ($74.3\text{SiO}_2 \cdot 14.8\text{Li}_2\text{O} \cdot 4.1\text{K}_2\text{O} \cdot 3.4\text{Al}_2\text{O}_3 \cdot 3.4\text{P}_2\text{O}_5$ in wt.%) showed the highest correlation. It had the largest “relative crystal area” with 78%, the highest crystal phase content of 42.7 wt.% as established by the Rietveld refinement and the highest strength with 680 MPa. Nevertheless, the determination of the “relative crystal area” is merely an estimate and other factors, such as the crystallite size, may equally influence the strength of the material.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Glass-ceramics have many different applications these days. Due to their low coefficient of thermal expansion, ceramics of the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Li}_2\text{O}$ system, for example, are used to produce telescope mirrors, cookware, fireplace windows and stove tops. Furthermore, glass-ceramics are characterized by their interesting mechanical properties [1]. Examples of these glass-ceramics include the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ system, the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Na}_2\text{O}$ system and the $\text{SiO}_2\text{--Li}_2\text{O}$ system, which will be examined in the present publication. The highest possible strength of the glass-ceramics is attained in different ways, which will be discussed.

In the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Na}_2\text{O}$ system, high strength is obtained by two different means: that is, either by coating the material with a glass, which has a lower coefficient of thermal expansion than the glass-ceramic [1,2], or by exchanging potassium for sodium ions. The ion exchange process takes place in a high-temperature bath (52 wt.% KCl and 48 wt.% K_2SO_4 at 730 °C). In this process, a 30 μm layer develops from the surface, in which kalsilite forms. Furthermore, the kalsilite grows on the edges of nepheline crystals. Strengths of up to 1450 MPa have been attained after an eight-hour immersion period [3].

In the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ system the strength increase is achieved through the precipitation of crystal phases that have a higher coefficient of thermal expansion than the residual glass phase [4–8]. The crystal phase in question is the low-quartz solid solution, which is dependent on the composition of the base glasses, the crystallization temperature [6] and time [9]. Moreover, the SiO_2 concentration within the quartz solid solution crystals is an important parameter, as it determines the modification of the quartz solid solution crystal phase [10]. Therefore, the high-quartz solid solution, which contains approx. 60 mol% SiO_2 and 20 mol% each of MgO and Al_2O_3 , is precipitated at comparatively low crystallization temperatures [9]. The incorporation of MgO and Al_2O_3 is responsible for rendering the high-quartz solid solution stable at room temperature: It does not change into a low-temperature modification, as is the case with pure quartz (quartz inversion at 573 °C) [6]. If the crystallization temperature increases, however, the concentration of SiO_2 in the quartz solid solution increases, while that of MgO and Al_2O_3 decreases to <2 mol%. Consequently, the high-temperature modification loses its stability and the high-quartz solid solution transforms to a low-quartz solid solution during cooling [10]. This transformation has the effect of toughening the glass-ceramics. As a result, strengths of up to 475 MPa [8] have been obtained. Furthermore, a Young's modulus of up to 140 GPa [5], a Vickers hardness of up to 13.3 GPa [8] and fracture toughness of up to 4.3 $\text{MPa} \cdot \text{m}^{1/2}$ [6] have been achieved.

* Corresponding author. Tel.: +423 235 36 17; fax: +423 239 46 17.

E-mail address: marc.dittmer@ivoclarvivadent.com (M. Dittmer).

In the $\text{SiO}_2\text{-Li}_2\text{O}$ system, the microstructure is responsible for producing the high-strength properties. The crystal structure is achieved by controlled nucleation and subsequent crystallization, which has been examined in stoichiometric [11–17] and in non-stoichiometric multi-component compositions [18–20]. The excellent properties attained with this glass-ceramic are widely recognized. As early as in 1973, glass-ceramics exhibiting strengths of 100 to 300 MPa [21,22] and fracture toughness of 2 to 3 $\text{MPa}\cdot\text{m}^{1/2}$ [23] were produced. Subsequently, these properties were further improved and combined with other characteristics, such as optical properties [24–28]. The $\text{SiO}_2\text{-Li}_2\text{O-Al}_2\text{O}_3\text{-K}_2\text{O-P}_2\text{O}_5\text{-ZrO}_2$ system is an example of such a composition. The glass-ceramic was produced from a monolithic glass-ceramic block by means of controlled nucleation and crystallization. It demonstrated strengths of 450 to 740 MPa. The commercial products exhibited a flexural strength between 530 and 617 MPa [29]. The laboratory standards demonstrated flexural strengths of up to 740 MPa and a fracture toughness of 3.13 $\text{MPa}\cdot\text{m}^{1/2}$, which was determined by using the Vickers test [26,30,31]. Furthermore, fracture propagation in lithium disilicate glass-ceramics was compared with that of leucite- and apatite-based glass-ceramics. These studies showed that crack growth occurs only in the glass phase and it is stopped by the crystals. When the crack tip is deflected, a new surface has to be created, which requires energy. This process is responsible for producing the high toughness of the material [32]. These results demonstrate that the microstructure formation of lithium disilicate glass-ceramics considerably influences the material's mechanical properties. In other words, the crystal size or rather the crystal phase content of lithium disilicate has a significant influence on the strength values that can be achieved. This has been shown on the basis of DICOR® MGC glass-ceramics from the chemical system of $\text{SiO}_2\text{-MgO-K}_2\text{O-F}$. The results showed that a diameter of approx. 4.5 μm leads to maximum strength values, while smaller or larger diameters produce lower strength values [33].

The aim of this paper is to compare the microstructure formation of the $\text{SiO}_2\text{-Li}_2\text{O}$ and the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ systems and to demonstrate a possible correlation between the microstructure of the $\text{SiO}_2\text{-Li}_2\text{O}$ system and the attainable strengths of four different compositions. For this purpose, the crystal content of the cut specimens was estimated on the basis of scanning electron micrograph images and Rietveld refinement.

2. Experimental

The glass of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system with the composition of $21.2\text{MgO}\cdot 21.2\text{Al}_2\text{O}_3\cdot 51.9\text{SiO}_2\cdot 5.7\text{ZrO}_2\cdot 0.2\text{Y}_2\text{O}_3$ in mol% was melted in batches of 100 to 200 g in an uncovered platinum crucible: The raw materials 4 $\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$, SiO_2 and ZrO_2 (TZ-3Y, Tosoh, Japan) were used. After a holding time of 3 h at 1590 °C, the glass was cast into water, dried and crushed and melted for another 3 h at 1590 °C for improved homogenization. Subsequently, the raw melts were cast into shape in a brass mold and transferred to a cooling furnace, which had been preheated to 810 °C. Then, they were cooled to room temperature with approx. 3 K/min. From the cooled blocks samples with approx. 5 mm × 5 mm × 10 mm were cut. These were crystallized in the temperature range of 950 to 1150 °C (in 50 K steps; heating rate of 5 K/min) for 3 h. In order to determine the crystal phases, the samples were powdered and examined with the help of X-ray diffraction with $\text{Cu}_{K\alpha}$ radiation in the 2θ -range of 10 to 60° (D5000, Siemens, Munich, Germany).

Four glasses from the $\text{SiO}_2\text{-Li}_2\text{O}$ system (Table 1) were melted in 100 g batches. For this purpose, the raw materials SiO_2 , Li_2CO_3 , $\text{AlOOH}\cdot\text{H}_2\text{O}$, $\text{Al}(\text{PO}_3)_3$, K_2CO_3 and Y_2O_3 were melted in a Pt–Rh crucible at 1450 °C for 40 min. The raw melts were cast in water, dried and crushed. Subsequently, the frits were melted at 1500 °C for 90 min to improve their homogeneity. Next, the temperature was lowered to 1400 °C. This temperature was maintained for 30 min. After the

Table 1

Composition of the 4 glasses of the $\text{SiO}_2\text{-Li}_2\text{O}$ system determined by XRF in wt.%.

	A	B	C	D
SiO_2	73.2	72.8	74.3	70.1
Li_2O	15.4	15.1	14.8	14.8
K_2O	4.0	3.8	4.1	3.8
Al_2O_3	3.4	3.3	3.4	3.5
P_2O_5	4.0	5.0	3.4	3.2
Y_2O_3	0	0	0	4.6

samples had been cast, they were transferred to a cooling furnace, which had been heated between 480 and 500 °C. The temperature was maintained for 10 min and lowered to room temperature with approx. 3 K/min. Then, the samples (12 mm × 14 mm × 30 mm) were crystallized as described in Table 2.

The chemical composition of the specimens was determined by means of X-ray fluorescence (XRF) with a Siemens SRS 3000, while the lithium oxide content was established with an atomic absorption spectrometer (AAS).

In order to determine the crystal phases, specimens 12 mm × 14 mm × 2 mm were produced from the blocks. These samples were polished and examined using an AXS D5005 diffractometer in the 2θ -range of 10 to 60.313° in 0.014° steps with a step time of 0.5 s. Furthermore, the 4 samples were ground to <90 μm and mixed with Al_2O_3 , which served as an internal standard, in order to conduct an additional Rietveld refinement. Shortly before the analysis, the mixture was suspended in acetone and dried for improved homogenization of the two powders, and another X-ray diffraction pattern was recorded with a STOE STADI P diffractometer with $\text{Cu}_{K\alpha}$ radiation in the 2θ -range from 2 to 99.490° in steps of 0.01° with a step time of 80 s. The error of the Rietveld-refinement was about 0.15 wt.%.

The microstructure of the specimens was examined by scanning electron microscopy (SEM). For this purpose, the samples were heat treated according to the methods shown in Table 2. Subsequently, the surface of the samples was polished to a roughness of 0.5 μm and etched with 40-percent HF steam for 30 s.

The crystal surfaces were determined on the basis of the SEM images. The glass surfaces of each composition were applied to a transparency in black (negative image) which is subjective and depends on the observer. This leads to the largest error of about 2%. This transparency was scanned in and calibrated to the scale of the SEM image using a program called "Analysis" version 5.1, Olympus Soft Imaging Solutions GmbH, Germany. Subsequently, the glass phase was redrawn on the computer based on the SEM images and the contrast was adjusted. The percentage of glass or crystal surface was determined on the edited image using the "Analysis" program. In a further step, the crystals were classified. For this purpose, the crystals were traced on the basis of the SEM image and the superimposed negative image. This transparency was scanned in and calibrated to the scale of the SEM image using the "Analysis" program. The image was edited again to obtain an exact picture of the crystal shapes and sizes.

The biaxial samples were fabricated according to ISO 6872. After an initial crystallization process, biaxial specimens were milled from glass blocks (14 mm × 12 mm × 30 mm) using the CEREC system (Sirona). In the second step, the samples were fully crystallized and then polished (1st side: 125 $\mu\text{m}/15$ N per sample; 10 min 70 $\mu\text{m}/15$ N per sample; 2nd side: 125 $\mu\text{m}/15$ N per sample; 10 min 70 $\mu\text{m}/15$ N per sample; 10 min 15 μm , 15 N per sample). The final thickness of the samples was 1.20 mm ± 0.2 mm. The biaxial flexural strength was examined using a universal testing apparatus (Zwick 1456).

3. Results

Fig. 1 shows the X-ray diffraction pattern of a glass-ceramic from the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system featuring the nucleating agent ZrO_2 . The glass was crystallized for 3 h at 1000 °C. The main crystal phase

Download English Version:

<https://daneshyari.com/en/article/1481125>

Download Persian Version:

<https://daneshyari.com/article/1481125>

[Daneshyari.com](https://daneshyari.com)