Original Paper

Microstructural development of a P_2O_5-modified cordierite glass ceramic during sintering

Part 2. Densification experiments[1])

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The non-isothermal sintering of a P_2O_5-modified cordierite glass powder was investigated using sintering dilatometry, DTA and x-ray diffractometry. A typical densification curve as obtained by dilatometry with a constant heating rate is discussed. To clarify the dependence of the final degree of porosity on the heating rate additional porosity measurements were carried out on selected specimens using a stereological image processing system.

The porosity exhibits a distinct minimum for a heating rate of 15 K/min. This effect is discussed based on a variation of the effective sintering interval which ranges from T_g of the glass to the onset temperature of crystallization. Together with the crystallization behaviour, as given in part 1 of this paper, a schematic description of the microstructural development is presented.

Entwicklung der Mikrostruktur einer P_2O_5-modifizierten Cordieritglaskeramik während des Sinterns
Teil 2. Verdichtungsversuche

Das nichtisotherme Sinterverhalten eines P_2O_5-modifizierten Cordieritglaspulvers wurde mit Sinterdilatometrie, DTA und Röntgendiffraktometrie untersucht. Ein typisches, mit einer konstanten Aufheizrate im Sinterdilatometer gemessenes Verdichtungsverhalten wird diskutiert. Zur Klärung der Abhängigkeit der verbleibenden Porosität von der beim Sintern verwendeten Aufheizrate wurde an ausgewählten Proben zusätzlich die Porosität stereologisch mit einem Bildverarbeitungssystem untersucht.

Dabei ist ein Minimum der Porosität bei Verwendung einer Aufheizrate von 15 K/min zu beobachten. Dieser Zusammenhang zwischen Porosität und Aufheizrate wird auf der Grundlage der im Sinterintervall, das im vorliegenden Fall im Temperaturbereich zwischen T_g des Glases und dem Beginn der Kristallisation liegt, auftretenden Änderungen diskutiert. Zusammen mit den in Teil 1 dieser Arbeit beschriebenen Ergebnissen des Kristallisationsverhaltens wird eine schematische Darstellung der Gefügeentwicklung vorgestellt.

1. Introduction

Systematic investigations into the sintering of stoichiometric cordierite glass were conducted as early as 1966 [2]. It is well-known that a stoichiometric cordierite glass exhibits only a very poor sinterability [3]. Therefore, the use of modified cordierite glasses is very common. Especially due to the low dielectric constant, several studies on modified glasses were carried out recently (e.g. [4 and 5]). For the present investigation a glass composition of the primary cordierite phase field (with P_2O_5 additions) was selected. This composition has already been described by Rabinovich [6] as a cordierite glass ceramic with good sinterability and high strength.

The aim of this study is to investigate the sintering process and to relate it to the crystallization behaviour given in [1]. Using the information from both parts a model for the microstructural development during sintering is derived which is presented in this part of the study.

2. Experimental procedure

The batch of nominal composition (in wt%) 52.5 SiO_2, 24.9 Al_2O_3, 18.1 MgO and 4.5 P_2O_5 was melted in a platinum crucible at 1550 °C for 2 h. After quenching, the glass was crushed and milled to an average particle size of 2.5 µm. Compacts were cold-isostatically pressed at 630 MPa for 1 min.

Dilatometric sintering investigations were carried out with a self-constructed vertical dilatometer. The specimens were heated in a platinum resistance furnace under a slightly flowing air atmosphere. The temperature was controlled with a Pt/PtRh thermocouple placed close to the specimen. Length changes were measured with a calibrated inductive displace-

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[1]) Rudolph, T.; Szabó, D. V.; Pannhorst, W. et al.: Microstructural development of a P_2O_5-modified cordierite glass ceramic during sintering. Pt. 1. Microscopic characterization. Glastech. Ber. **64** (1991) no. 8, p. 218–224 [1].
[2]) Now with: Degussa AG, Hanau (FRG).
[3]) Now with: Daimler-Benz AG, Stuttgart (FRG).

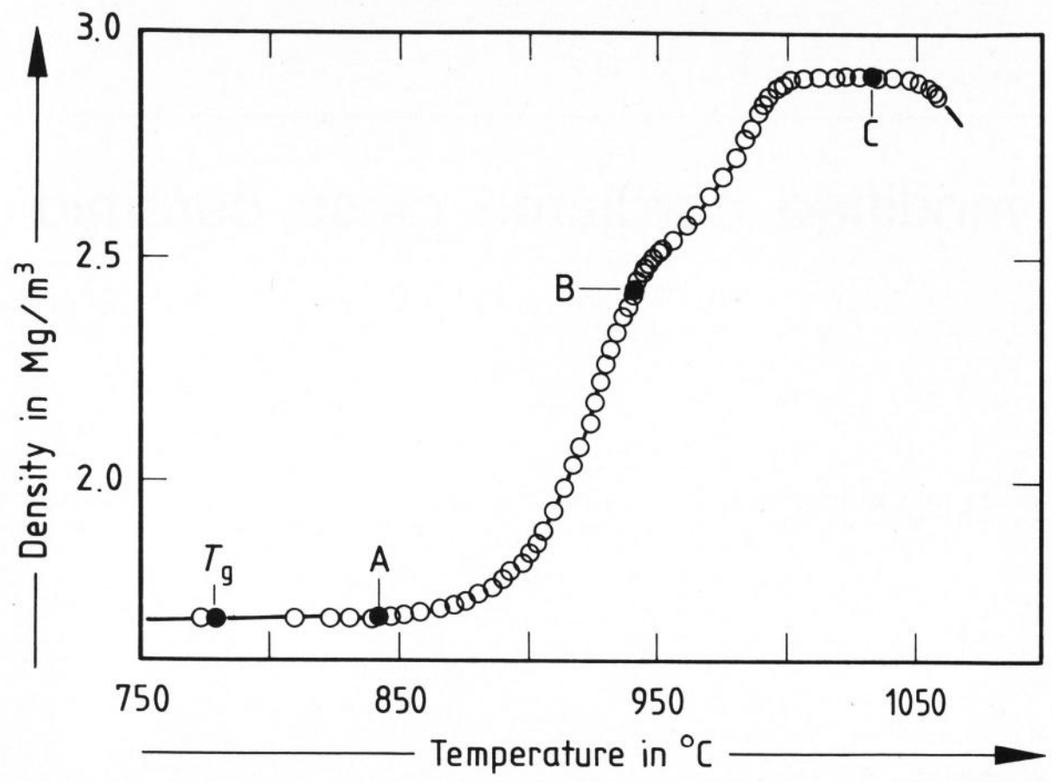
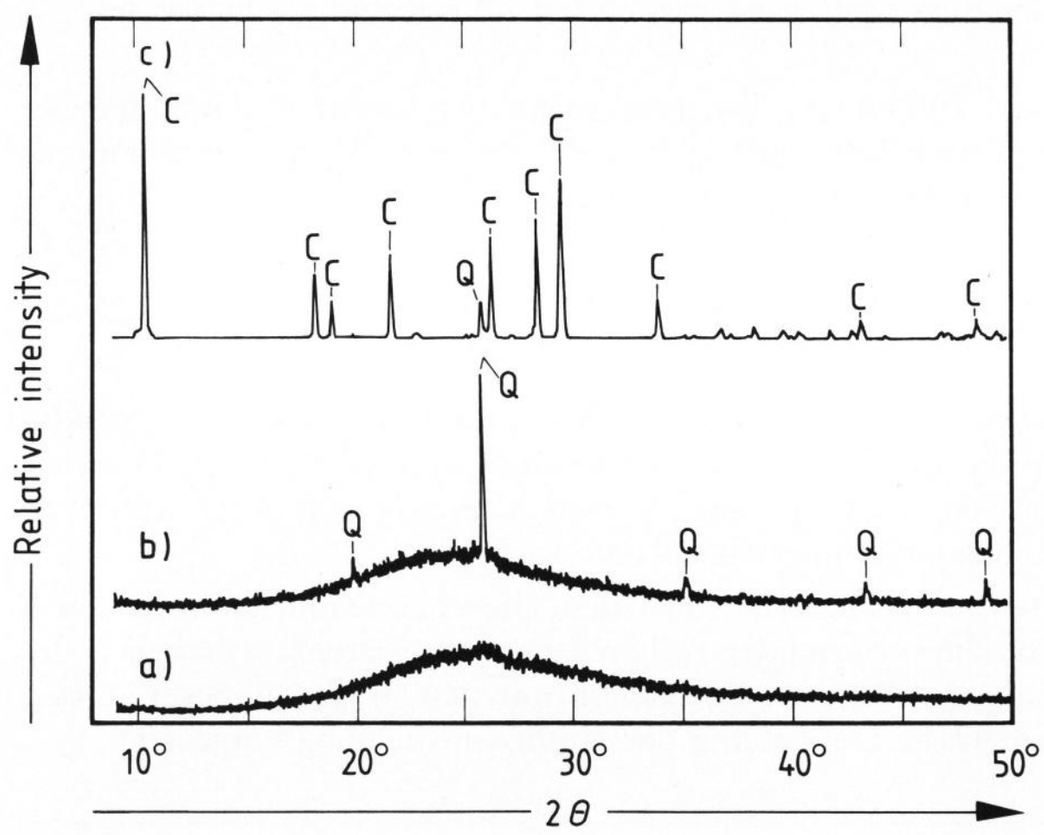


Figure 1. Density as a function of temperature for a P_2O_5-modified cordierite glass at a heating rate of 15 K/min recorded with a sintering dilatometer. A, B, and C indicate characteristic points in the shrinkage behaviour.



Figures 2a to c. XRD patterns of P_2O_5-modified cordierite glass specimens heated with a rate of 15 K/min and quenched from a temperature of a) 930 °C, b) 950 °C, c) 950 °C with 6 min annealing time. C: high cordierite, Q: high-quartz solid solution.

ment pickup. The density was calculated from the length changes assuming isotropic shrinkage of the specimens. Additional specimens for the stereological investigations were sintered in a $MoSi_2$-heated muffle furnace (Nabertherm GmbH + Co. KG, Lilienthal (FRG)), equipped with a programmable temperature controller (Eurotherm, Limburg (FRG)).

The stereological porosity measurements were performed with an Image Processing System (IPS) (SEM-IPS, Kontron GmbH, Eching (FRG)) hooked up to a Scanning Electron Microscope (SEM) (JSM-35 C, JEOL, Ltd., Tokyo (Japan)). Carefully ground and polished sections from sintered specimens were analyzed after manually adjusting the discriminating grey level of the IPS to the screen image of the specimens. For each specimen 10 micrographs were processed using around 600 magnifications. The fractional area of pores (A_{pore}/A_{total}), as seen in the SEM image, is then directly equal to the fractional volume of pores in the specimens (V_{pore}/V_{total}) [7].

Differential Thermal Analysis (DTA) experiments were performed with a Netzsch STA 429 Thermal Analyzer (Netzsch GmbH, Selb (FRG)). About 400 mg of powdered glass were taken for each run. The experiments were carried out in alumina crucibles under a slightly flowing air atmosphere (≈ 70 ml/min). Alumina powder was used as reference material.

X-ray investigations were performed by standard diffractometry (XRD) techniques. The radiation used was Cu−K_α. For data acquisition the specimens were scanned with a step width of 0.02° and a counting time of 1 s.

3. Results and discussion

3.1. Experiments with a constant heating rate

A typical densification curve for a constant heating rate of 15 K/min recorded with the sintering dilatometer is shown in figure 1. The shape of the curve leads to a division into three distinct regions, as indicated by the characteristic points A, B and C. The regions are as follows: a) the interval from the onset of the densification process to the decrease in densification rate (region from point A to B); b) the decrease in densification rate until densification stops (region between points B and C); c) a post-densification decrease in density (beyond point C).

In region A−B (from ≈ 840 to 940 °C) the curve shows a steep increase in sintering rate. In [1] it was shown that for a heating rate of 15 K/min up to a temperature of ≈ 920 °C no crystallization is observable. Therefore, the dominant sintering mechanism in the temperature interval from T_g at 780 °C to the onset of crystallization at 920 and even up to 940 °C is assumed to be the viscous flow of the glass. The steep increase in sintering rate is then due to the exponentially decreasing viscosity of the glass with progressing time and temperature. That region A−B extends to 940 °C and thus above the temperature for the onset of crystallization is explained by the small amount of crystalline phase which does not influence the densification behaviour.

For intermediate temperatures (region B−C from ≈ 940 to 1040 °C) the curve indicates a decrease of the sintering rate with increasing temperature. This effect is mainly due to the progressing crystallization which starts to reduce the densification rate due to viscous flow. The progressing crystallization is illustrated by using x-ray diffractometry (XRD, figures 2a to c). A specimen quenched from 930 °C (figure 2a) yields the typical diffraction pattern of glasses indicating that the total amount of crystalline phases is still below the detection limit. With a specimen quenched from 950 °C (figure 2b) still a high amount of glassy phase but also first signals from high-quartz

solid solution (high-quartz s.s.) as primary crystalline phase is detected.

At or above 950 °C (figure 2c) crystallization proceeds more rapidly as is demonstrated by the drastic increase in signal from crystal phases of a specimen annealed for 6 min at 950 °C. The material is still mostly glassy (as may be seen from figures 2a and e [1]). However, since the XRD is more sensitive to regular crystal lattices it offers a good possibility to study a crystallization process even with a small crystalline content in glasses. The main crystalline phase here is high cordierite with only minor amounts of high-quartz s.s. On further heating or annealing the glass continues to transform into cordierite, most likely with high-quartz s.s. as an intermediate phase.

At this point it seems noteworthy that the apparent second rise of the sintering rate in region B–C (starting ≈ 970 °C; figure 1) and the resulting high absolute density may be due to an erroneous dilatometric measurement. The small weight force (≈ 70 mN) applied by the displacement pickup of the dilatometer onto the specimen as well as the specimen's own weight may have led to an additional non-isotropic shrinkage of the specimen in vertical direction. These effects are of increasing importance with increasing temperature due to the rapidly decreasing viscosity of the glass. The viscosity, η, for the glass used in this study, as measured by bar bending viscosimetry, may be expressed by equation (1)

$$\lg \eta = -3.427 + \left(\frac{5367}{T - 730.3}\right) \qquad (1)$$

with T = absolute temperature and the viscosity, η, being expressed in units of dPa s. Neglecting the crystalline phases, a viscosity value of $1.1 \cdot 10^7$ dPa s is calculated for a temperature of 970 °C; this low viscosity may account for a deformation of the specimen even at small loads. The low viscosities for temperatures above ≈ 970 °C, therefore, may result in a higher apparent vertical shrinkage of the specimen in the dilatometric experiment, especially for the high heating rate of 15 K/min, than would have been observed when using different techniques (i.e. density determination by Archimedes technique, stereological porosity determination).

Above approximately 980 °C the progressing crystallization inhibits densification by viscous flow more and more until densification decreases to zero at point C. At further heating the densification rate becomes even negative so that the density has attained a maximum at point C. TEM investigations [1] clearly exhibit that the density maximum is related to the formation of a crystal skeleton around the former glass particle surfaces, preventing further densification by viscous flow. Moreover, the advancing crystallization of the glass within the crystal skeleton results in an overall decrease in density. This effect may be due to the lower density of crystalline cordierite (2.512 Mg m^{-3}) compared to the density of the glass used in this study (≈ 2.700 Mg m^{-3}).

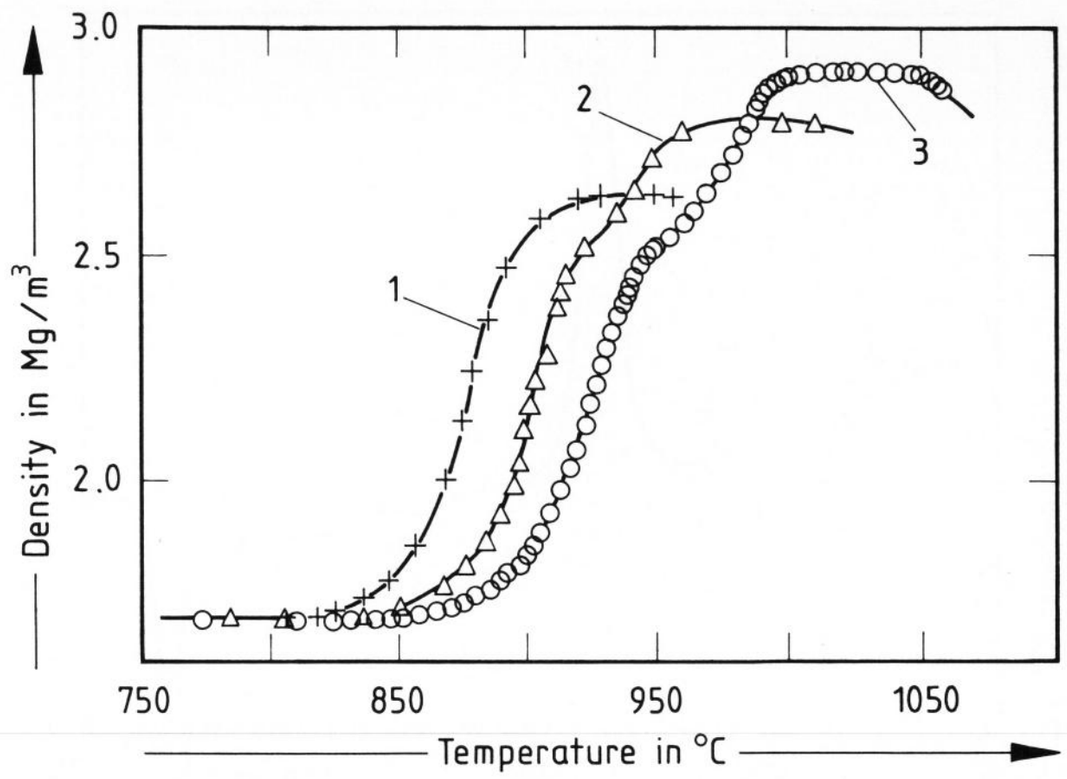


Figure 3. Dilatometric densification curves of a P_2O_5-modified cordierite glass recorded for different heating rates (in K/min), curve 1: 1.5, curve 2: 8.0, curve 3: 15.0.

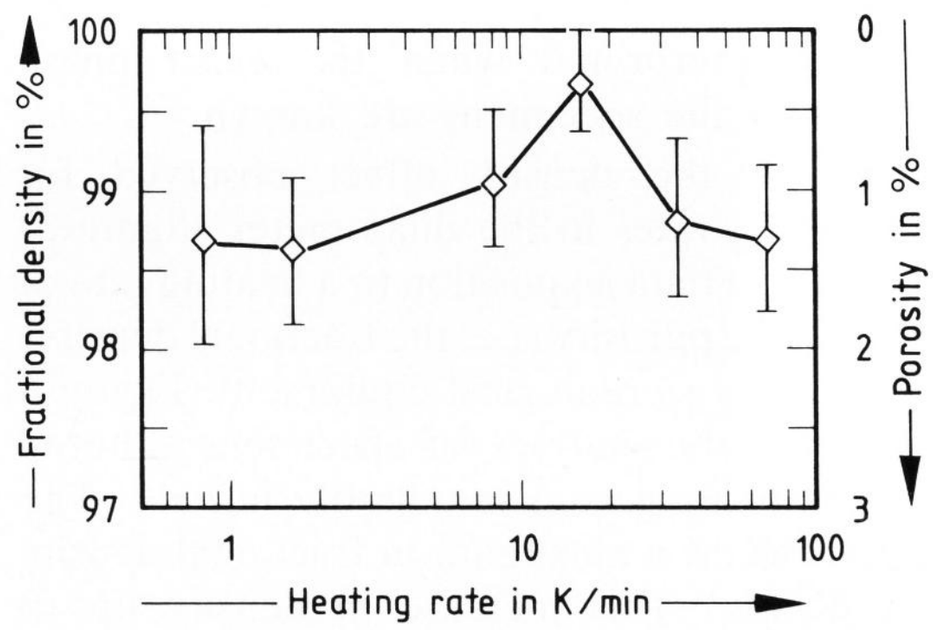


Figure 4. Fractional density and porosity data of P_2O_5-modified cordierite glass specimens heated with rates from 0.8 to 70 K/min showing the densification maximum. The data were obtained using a stereological image processing system.

3.2. Experiments with different heating rates

To study the dependence of densification on different heating rates additional glass specimens were sintered in the sintering dilatometer with heating rates of 1.5, 8 and 15 K/min (figure 3). Increasing heating rates lead to a shift of the densification curves to higher temperatures. Additionally, an increase in final density is suggested by the increase of the maximum density values in the densification curves.

Unfortunately, the density difference between crystalline cordierite and the glass used in this study makes it impossible to distinguish by a dilatometric measurement or an absolute density measurement (e.g. by Archimedes method) between low absolute final densities due to a high amount of porosity (i.e. a low fractional density) or due to a high crystal-to-glass ratio. Therefore, such density determinations

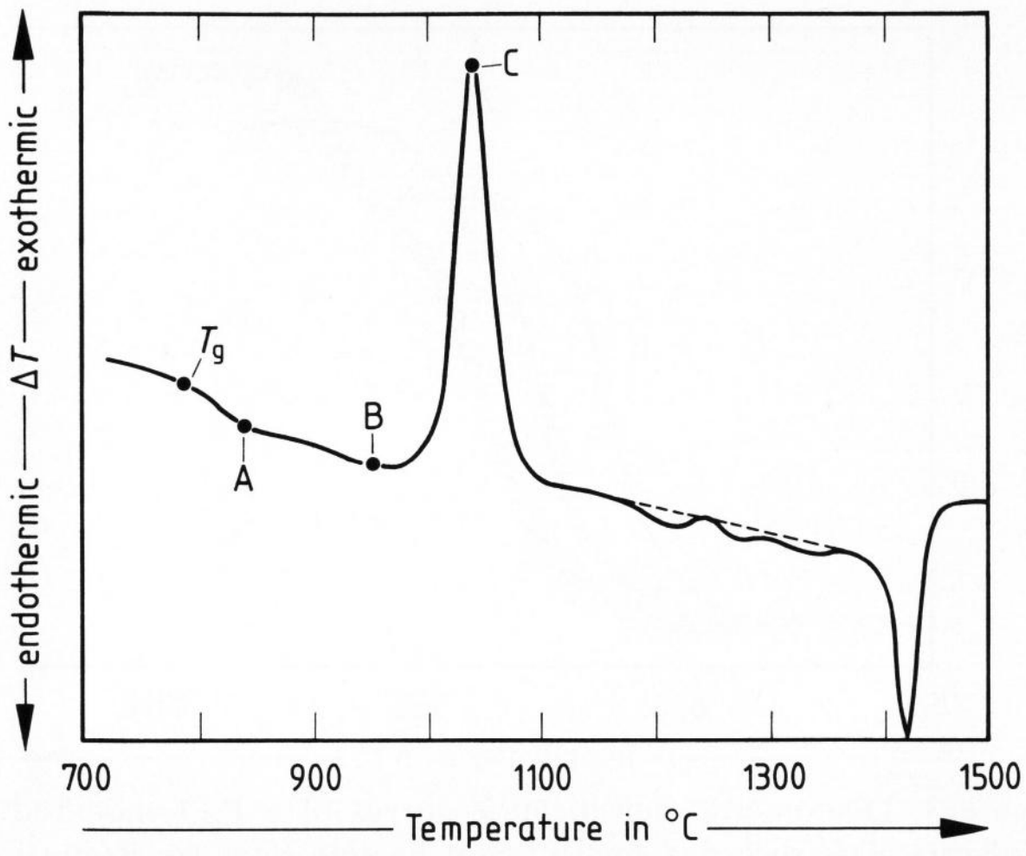


Figure 5. DTA curve of a P_2O_5-modified cordierite glass recorded at a constant heating rate of 15 K/min.

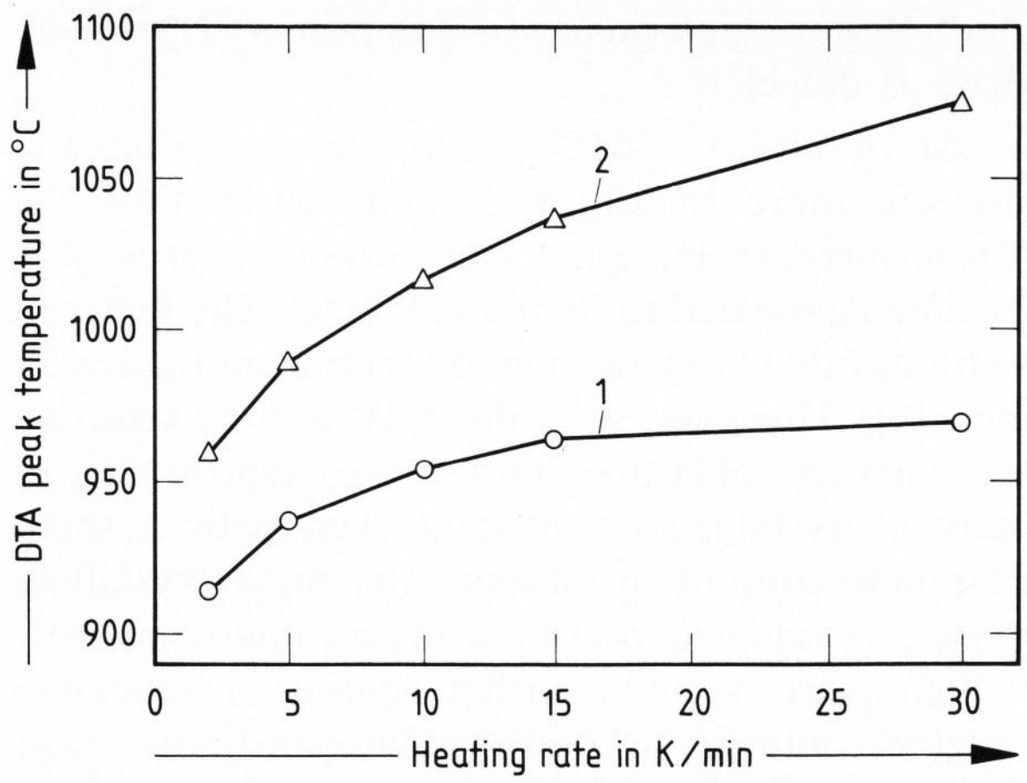


Figure 6. Shift of the starting (curve 1) and maximum (curve 2) temperatures of the exothermic peak of a P_2O_5-modified cordierite glass in the DTA as a function of the heating rate.

can only be interpreted when the exact phase compositions of the specimens are known.

To confirm the density effect observed for different heating rates in the dilatometer (figure 3) and to extend the data acquisition to a heating rate of 70 K/min the true porosity (i.e. the fractional density) was studied using stereological equipment. Figure 4 shows the porosity analyses of specimens sintered with different heating rates in a muffle furnace. The data clearly exhibit a maximum in fractional density around 15 K/min. This increase in density up to 15 K/min confirms the dilatometric results. Unexpectedly, at heating rates of 35 and 70 K/min a decrease in fractional density of the specimens is obtained. A discussion of these results is presented in section 3.3. together with the results of the DTA experiments.

3.3. DTA experiments

A common way to study phase changes is the use of DTA. Figure 5 shows the DTA curve for a heating rate of 15 K/min, which may be directly correlated to the densification curve in figure 1. After a small endothermic effect around 780 °C, which indicates T_g, the temperature interval between points A and B shows no signs of reactions or phase changes. At 964 °C a large exothermic peak starts which is due to the crystallization of the glass. The onset of the peak is in good agreement with point B in the densification curve.

As is already discussed in part 1 [1] the exothermic peak is actually caused by several processes which overlap in this region. Here, the crystallization of the hexagonal high-quartz s.s. as well as the instantaneous precipitation of hexagonal high cordierite and the transformation of high-quartz s.s. to high cordierite give an effect. At higher temperatures first three small peaks and then one large endothermic peak are observed. While the first small peak is attributed to the melting of $3\,MgO \cdot P_2O_5$ [1] at 1184 °C, the other small endothermic peaks are believed to indicate other, unknown melting reactions of minor components. The large peak with the onset at 1360 °C is believed to be due to the melting point of the cordierite phase being lowered by contact with other phases such as $3\,MgO \cdot P_2O_5$.

Further information is deduced from DTA experiments conducted with different heating rates. In addition to the DTA curve recorded with 15 K/min, runs at 2, 5, 10, and 30 K/min were carried out. As expected from previous results the exothermic peak shifts towards higher temperatures with increasing heating rate (figure 6). Moreover, higher heating rates also lead to a broadening of the peak. This effect results in a smaller shift of the peak starting temperatures as compared with the peak maximum temperatures.

With this difference in the shift of both characteristic DTA peak temperatures an explanation for the dependence of the final fractional density on the heating rate (as described in section 3.2.) may be obtained. First of all the reason for the increase in density with increasing heating rate (up to 15 K/min) is believed to result from a general shift of the crystallization process to higher temperatures as can easily be verified by studying the shift of the exothermic peak in analogous DTA experiments. This leads to an actual "broadening of the sintering interval" between T_g and the onset of crystallization. While this shift of the densification process to higher temperatures partly compensates this effect, the overall broadening is still in effect.

However, the shift of the peak maximum temperature in the DTA is unsuitable to explain the following decrease in fractional density using heating rates of 35 and 70 K/min (figure 4). The peak maximum temperature continuously increases for all

heating rates investigated. A more suitable measure for the width of the sintering interval is the peak starting temperature in the DTA, which marks the onset of crystallization. It shows a different behaviour: While the peak starting temperature also increases steadily with heating rates up to 15 K/min, this increase becomes very small using 35 and 70 K/min. At higher heating rates the sintering interval thus effectively decreases due to the shift of the densification curves to higher temperatures and a rather constant onset of crystallization. This results in a termination of the densification at higher degrees of porosity and leads to lower fractional densities.

Finally combining the sintering, DTA and XRD experiments presented here with the microscopical investigations already presented in [1], a schematic description of the development of the microstructure can be obtained. Figures 7a to e summarize the characteristic densification steps for a heating rate of 15 K/min, which are viscous flow sintering (starting ≈ 840 °C), crystallization onset and decrease in sintering rate (starting at 920 and 940 °C, respectively), and crystal skeleton formation as the end of densification (≈ 1030 °C) followed by an oriented crystallization.

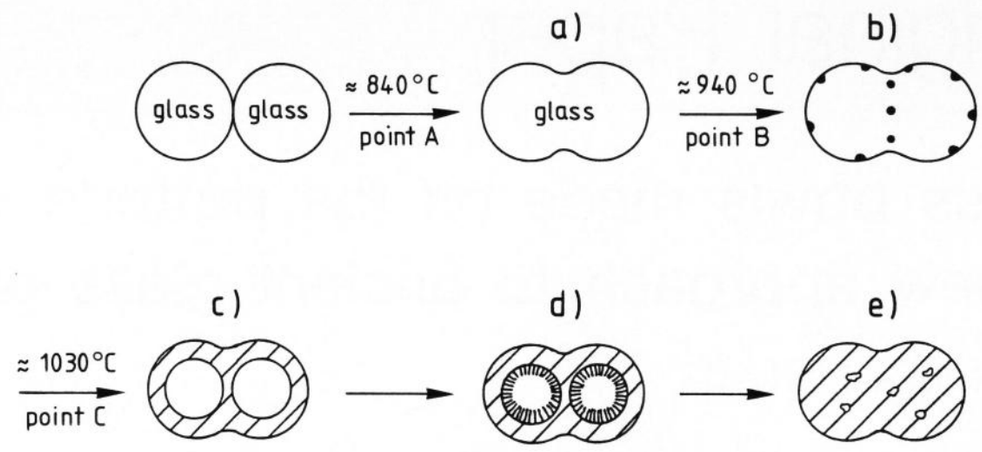
4. Summary and conclusions

The sintering experiments along with the microscopic studies lead to the following sequence for the development of microstructure and phases:

For a glassy powder compact heated at a rate of 15 K/min the densification starts around 840 °C (point A, figure 1). Since no signs of crystallinity were detected below 920 °C using DTA, XRD and microscopy [1], the sintering effect is assumed to result from viscous flow of the glass.

Between points B and C the decrease in densification rate is due to three overlapping processes: a) the beginning crystallization, which results in obstacles for the viscous flow of the glass, accounts for the main effect; b) starting with the formation of closed pores the diffusion of gases through the glass also retards the densification; c) due to the lower density of crystalline cordierite compared to the parent glass the increase in density due to densification may be partially compensated by the decrease in density due to the phase transformation.

Beyond point C the phase transformation becomes dominant and the density therefore decreases slightly, thus leading to a maximum in the densification curve. A crystal skeleton develops at the original particle surfaces due to the so-called "memory effect". Beyond this point crystallization progresses with a lamellar nature. While the orientation of the crystals is random during the early stage of crystallization, impingement on other crystals soon leads to a microstructure with the *c* axis of neighbouring hexagonal crystals oriented parallel.



Figures 7a to e. Schematic description of the microstructural development with temperature for a heating rate of 15 K/min; a) viscous flow sintering, b) onset of crystallization and decrease in densification rate, c) formation of a crystal skeleton and end of densification, d) oriented crystallization, e) high-cordierite body with a multicomponent intergranular phase.

Higher heating rates cause a shift of the crystallization as well as of the densification curves to higher temperatures. For heating rates up to 15 K/min this results in an effective "broadening of the sintering interval" of the glass. Consequently, the remaining porosity is lowered with increasing heating rate. However, for heating rates above 15 K/min the onset of crystallization almost remains constant. Therefore, the sintering interval becomes effectively narrower which results in an increase in porosity.

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The authors want to thank Mrs. Christine Weis for the careful porosity measurement using the IPS.

5. References

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6. Correction

T. Rudolph; D. V. Szabó; W. Pannhorst et al. Pt. 1. Microscopic characterization. Glastech. Ber. **64** (1991) no. 8, p. 218–224.

Reproducing figure 10 (p. 223) a mistake was made: The phase diagram is reported in wt%, not in mol%. In the caption the reference should read [7] instead of [6].

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