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Sintering and crystallization of volume- and surface-modified cordierite glass powders

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The sintering and crystallization behaviour of a series of cordierite-type glass powders with varying substitution of Na_2O for MgO was compared with that of glass powders subjected to an $Mg^{2+}2Na^{+}$ ion-exchange treatment. The ion-exchange modifies only the properties of a 3–4 μm thick surface layer on the glass grains. Whereas the bulk substitution results in a decrease in the glass transition temperature, T_g, the surface modification shows only a small influence on the overall T_g of the ion-exchanged glass. Both glass powder series show, however, a temperature decrease of the start of sintering with increasing Na_2O content which demonstrates that only the viscosity of a surface layer is decisive for the start of sintering. The sintering range is enlarged to higher temperatures through the suppression of the crystallization of β-quartz solid solution. The surface-modified glass powders show strong cordierite crystallization at constant temperatures around 1000 °C, whereas in the bulk-modified glass powders, the temperature of cordierite crystallization increases and the total amount of cordierite decreases with increasing Na_2O content.

1. Introduction

It is well known that glass powders sinter by a viscous flow mechanism. The basic theoretical equations derived by Frenkel [1] and MacKenzie and Shuttleworth [2] show that sintering can be enhanced by either reducing the grain size of the powder or by lowering the viscosity of the glass. The latter can be achieved by either increasing the sintering temperature or by chemical modification of the glass composition. In many glass systems, elevation of the sintering temperature is limited by the beginning of crystallization, which results in a drastic increase of the viscosity and thus hinders further sintering. The surface of a ground glass powder is characterized by a high number of flaws or other heterogeneities which can act as nucleation sites. Therefore, in most glasses the crystallization is initiated at the surfaces [3, 4].

The problem of interacting sintering and crystallization is encountered, for example, in the case of cordierite-type ($Mg_2Al_4Si_5O_{18}$) glass-ceramics. In this system the sintering range is overlapped by the crystallization range of the metastable precursor β-quartz solid solution (β-quartz$_{ss}$) which makes it very difficult to densify a stoichiometric cordierite glass powder [5–8]. In order to control the crystallization behaviour and to lower the viscosity, the glass composition can be modified within the system $MgO–Al_2O_3–SiO_2$ or further components can be added. These are especially B_2O_3 and P_2O_5, but also Li_2O, Na_2O, K_2O, CaO, TiO_2, ZrO_2 and others [5, 6, 9–11]. Some additions like B_2O_3 and P_2O_5 or alkalis, with the exception of Li_2O, suppress the crystallization of β-quartz$_{ss}$ and thus help to extend the sintering range to higher temperatures.

All these chemical variations change the bulk composition of the glass powder although the nucleation and possibly also the sintering are processes which involve only a thin surface layer. Helgesson [12] recognized this and developed a method of chemical treatment which influences only the surface of the glass powder. This method consists essentially of an etching process in an NaOH solution in order to reduce heterogeneities, nuclei and flaws on the surfaces. This reduces the nucleation sites, retards crystallization and enlarges the sintering interval to higher temperatures. Other effects of the chemical treatment are the rounding of individual particles, a reduction of the grain size and an enlargement of the surface area. A stoichiometric cordierite glass powder treated this way crystallized at a temperature approximately 20 °C higher as compared with an untreated powder, and also showed enhanced sintering. However, this method cannot be applied to all glasses. The effect depends strongly on the composition of the glass, the chemical durability and the extent and the temperature of crystallization [13–15].

Another method to change the properties of the surfaces of a glass powder is to coat it with a thin layer of different composition. The coating could be achieved by heterogeneous precipitation of metal salts through pH changes or by hydrolysis of metal alkoxides in a powder dispersion. These processes have been applied predominantly on ceramic powders to increase the reactivity of the components and to improve the sintering behaviour [16–19], to improve the homogeneous distribution of sintering aids or the homogeneous distribution of second phases in composite materials [20–22] or to improve the surface properties of powders [23, 24]. A sol-gel coating technique of a glass powder was used in order to introduce crystallized ZrO_2 homogeneously into a low-melting glass enamel (sodium zinc borosilicate) without changing its firing temperature [25]. The sintering of a cordierite glass powder is improved by a thin ZrO_2 coating of the particles which also results in an homogeneous distribution of ZrO_2 in the composite glass-ceramic material [26].

In this study, the effects of another method of powder surface modification will be described. It is well known that alkali ions in a glass can be exchanged for other alkali ions in a molten salt bath. This process has been applied on many glass compositions in the past in order to modify the surfaces of bulk glass materials in a range between 10 and 100 μm [27–31]. The idea was to generate a high compressive stress in a thin surface layer which results in a considerable strengthening of the glass body.

Whereas for the interexchange of two alkali ions numerous data about the diffusion processes are available, only limited information exists about the exchange of an alkali and an alkali earth ion [32]. Owing to the higher valence state of the alkaline earth ion and its stronger bonding in the glass network, it seems reasonable to estimate the interdiffusion coefficients some orders of magnitude lower than those for the interdiffusion of two alkali ions. The penetration depth into the glass body would be much smaller for an alkali/alkaline earth exchange compared to an alkali/alkali exchange. The reduced diffusivity makes this type of exchange unsuitable to reach a substantial strengthening of large glass bodies. However, when the size of the glass body is drastically reduced down to a glass powder, the volume to surface ratio decreases and the alkali/alkaline earth exchange will have an observable effect on the properties of the powder. This study reports the effects of the substitution of Mg^{2+} by $2Na^+$ in a cordierite-type glass powder on its sintering and crystallization behaviour. In order to compare the effects of the chemical surface modification with a chemical volume modification, a series of cordierite-type glasses with differing MgO/Na_2O ratios has been investigated.

2. Experimental procedure

The starting glass for the ion-exchange experiments was of a cordierite composition. A small excess of MgO and SiO_2 over Al_2O_3 compared to stoichiometric cordierite was taken to lower the melting temperature and facilitate the glass preparation. The composition was (wt %) 14.6 MgO, 32.4 Al_2O_3, 53.0 SiO_2.

In order to investigate the effects of volume compositional modifications, a series of glasses was prepared wherein Na_2O was substituted for MgO. The Na_2O-containing end-member of this series has the composition (wt %) 20.8 Na_2O, 30.0 Al_2O_3, 49.2 SiO_2, which corresponds approximately to the composition of nepheline $NaAlSiO_4$. These glasses are indexed by their degree of substitution, S (mol %) with $S0$ being the pure magnesium and $S100$ being the pure sodium-containing glass.

As starting materials Na_2CO_3, $MgCO_3$ and Al_2O_3 (Merck, Darmstadt, FRG) and SiO_2 (Bremthaler Quarzwerke, Usingen, FRG) were used.

The cordierite composition, which was designed for the ion-exchange experiments, was melted at 1600 °C under constant stirring in a platinum crucible using r.f. induction heating. The mixtures of the S series were melted twice in a chamber furnace at 1600 °C for 3 h, quenched in water and crushed in an agate mortar. After quenching in water, all glass frits were ground in an agate ball mill to a grain size < 40 μm.

In order to obtain a constant range of grain sizes, all glass powders were suspended in water and fractionated using their sink velocity applying Stoke's law. For further experiments, only the fraction 10–40 μm was used. Pellets with a green density of $68 \pm 2\%$ were formed by cold isostatic pressing with a pressure of 500 MPa.

Concentrations of Na_2O and MgO were measured by means of atom absorption spectrometry (AAS) on a Philips (Eindhoven, The Netherlands) PYE Unicam SP9 equipment. A Netzsch TMA400 (Selb, FRG) differential thermal analysis (DTA) equipment was used to study the crystallization behaviour and to determine the glass transition temperature, T_g. The heating rate was 10 °C min^{-1} and corundum was used as inert substance. Phase analysis was performed on a Philips (Eindhoven, The Netherlands) PW 1050/1049 powder diffractometer. Shrinkage due to sintering was measured on a Netzsch (Selb, FRG) TMA402 quartz-glass dilatometer. The heating rate was 10 °C min^{-1} up to 700 °C and 1.5 °C min^{-1} between 700 and 1000 °C'. Densities were measured using the Archimedes method through weighing in air and in distilled water. Scanning electron microscopy (SEM) was performed on a Philips (Eindhoven, The Netherlands) SEM 505 microscope equipped with EDX on polished and HF etched samples.

Glass powder $S0$ was subjected to ion exchange with a salt mixture consisting of 70 mol % $NaNO_3$ and 30 mol % Na_2SO_4 in corundum crucibles. The sample of salt ratio was 1:5. The powders were treated for 2, 4, 6 and 8 h at 650 °C and afterwards quenched in air. The salt was removed with distilled water and the glass powders were washed several times with distilled water and 0.1 N HCl solution.

3. Results

3.1. Volume modification

The Na_2O and MgO contents of the as-prepared glasses of the series $S0$–$S100$, $S0$ being the pure magnesium and $S100$ being the pure sodium-containing glass, were verified by means of AAS in order to detect losses during the melting process (Fig. 1). In general, the Na_2O and MgO contents of the glasses were in good accordance with the prepared compositions. The MgO content was slightly below the expected values in the glasses with high MgO content, and in glasses containing a high concentration of Na_2O, some small Na_2O losses had occurred during the melting of the glasses.

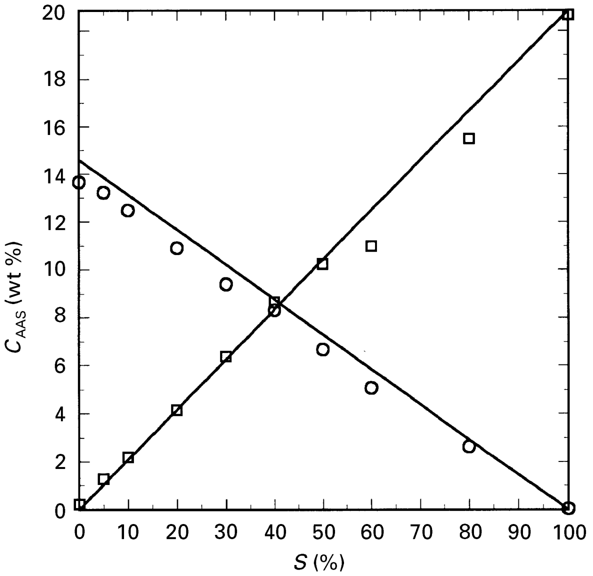

Figure 1 (○, □) Measured and (——) nominal concentrations, *c*, of (□) Na_2O and (○) MgO in the volume-exchanged glass powders.

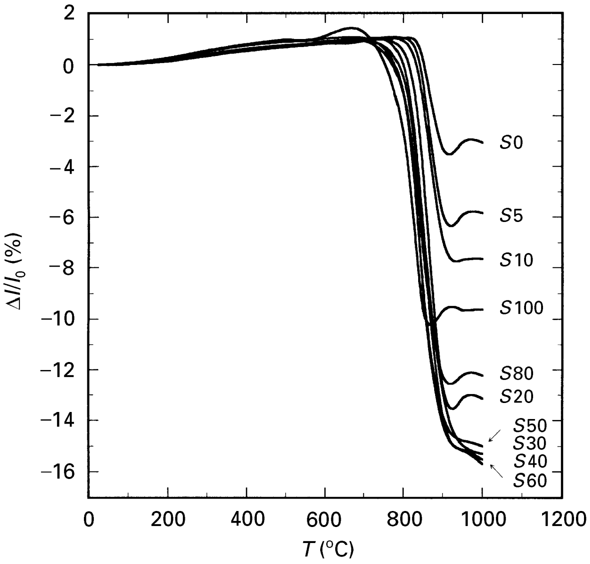

Figure 3 Sintering shrinkage $\Delta l/l_0$ of the volume-modified glass powders.

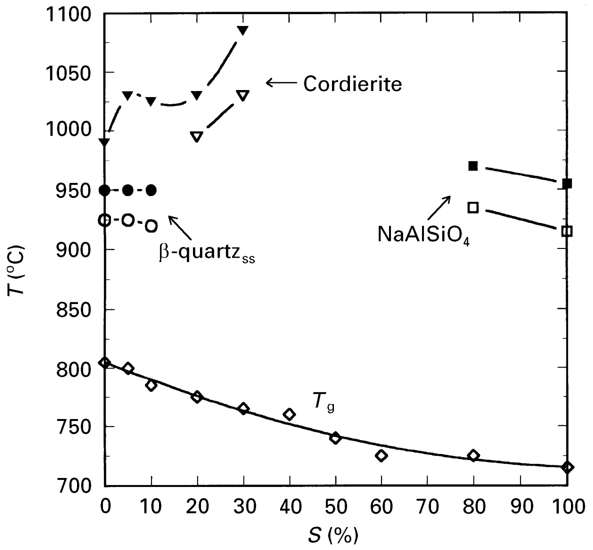

Figure 2 (●, ▼, ■) DTA peak maxima of β-quartz$_{ss}$, cordierite and nepheline crystallization and (□, ○) onset of crystallization as a function of Na_2O/MgO substitution *S*.

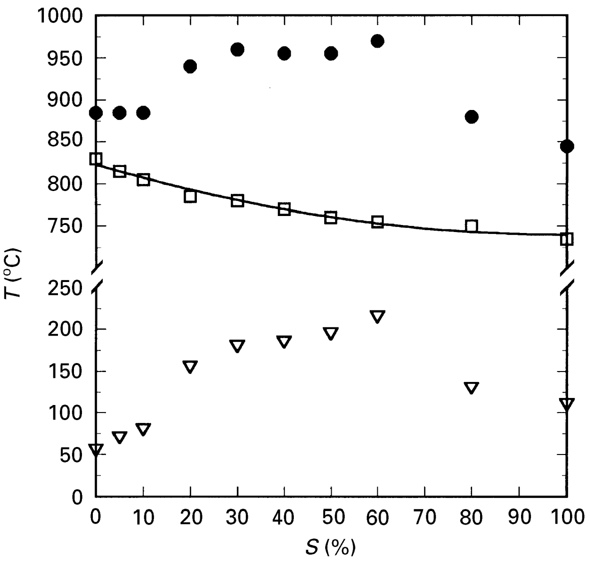

Figure 4 (□) Onset, T_i, and (●) end temperatures, T_{end}, of shrinkage and (▽) their difference, ΔT, as a function of Na_2O/MgO substitution, *S*.

The results of the DTA measurements can be seen in Fig. 2. The glass transition temperature decreases continuously with increasing Na_2O content from 805 °C to 715 °C. Between *S*0 and *S*100, four different ranges of crystallization can be distinguished. Between *S*0 and *S*10, two crystallization peaks of β-quartz$_{ss}$ and cordierite were recorded. At higher Na/Mg substitution up to *S*30 no β-quartz$_{SS}$ crystallization peak existed but only one cordierite peak. The third range lay between about *S*40 and *S*70 and showed no crystallization peak at all up to 1100 °C and in the last range, *S*70–*S*100, one nepheline ($NaAlSiO_4$) crystallization peak was recorded. The onset of crystallization was defined as the intersection of the tangent at the first peak flank with the horizontal line. The onset of crystallization remained constant at about 925 °C in the first range and shifted to 1030 °C between *S*10 and *S*30. In the high Na_2O-containing glasses *S*80 and *S*100, the onset of crystallization shifted again to lower temperatures. The temperature of the cordierite peak maximum increased from 990 °C to 1085 °C in the first and second range and the total amount of cordierite as estimated from XRD decreased simultaneously.

The shrinkage of the glass powders is plotted in Fig. 3. As expected, the sintering of a Na_2O-free glass powder (*S*0) was poor. With increasing substitution of Na_2O for MgO the shrinkage increased and reached a maximum in the glasses *S*30–*S*60. These glasses also showed strong deformation induced by the pressure of the dilatometer rod. The deformation explains shrinkage values $\gtrsim 12\%$ which can be expected at the most for samples with a green density of $\sim 68\%$ theoretical density. The shrinkage decreased again in the glasses *S*80 and *S*100. Fig. 4 shows a plot of the temperatures of the start and the end of the shrinkage as a function of the degree of Na_2O/MgO substitution. The temperature of the start of the shrinkage decreased continuously with increasing Na_2O content by about 100 °C

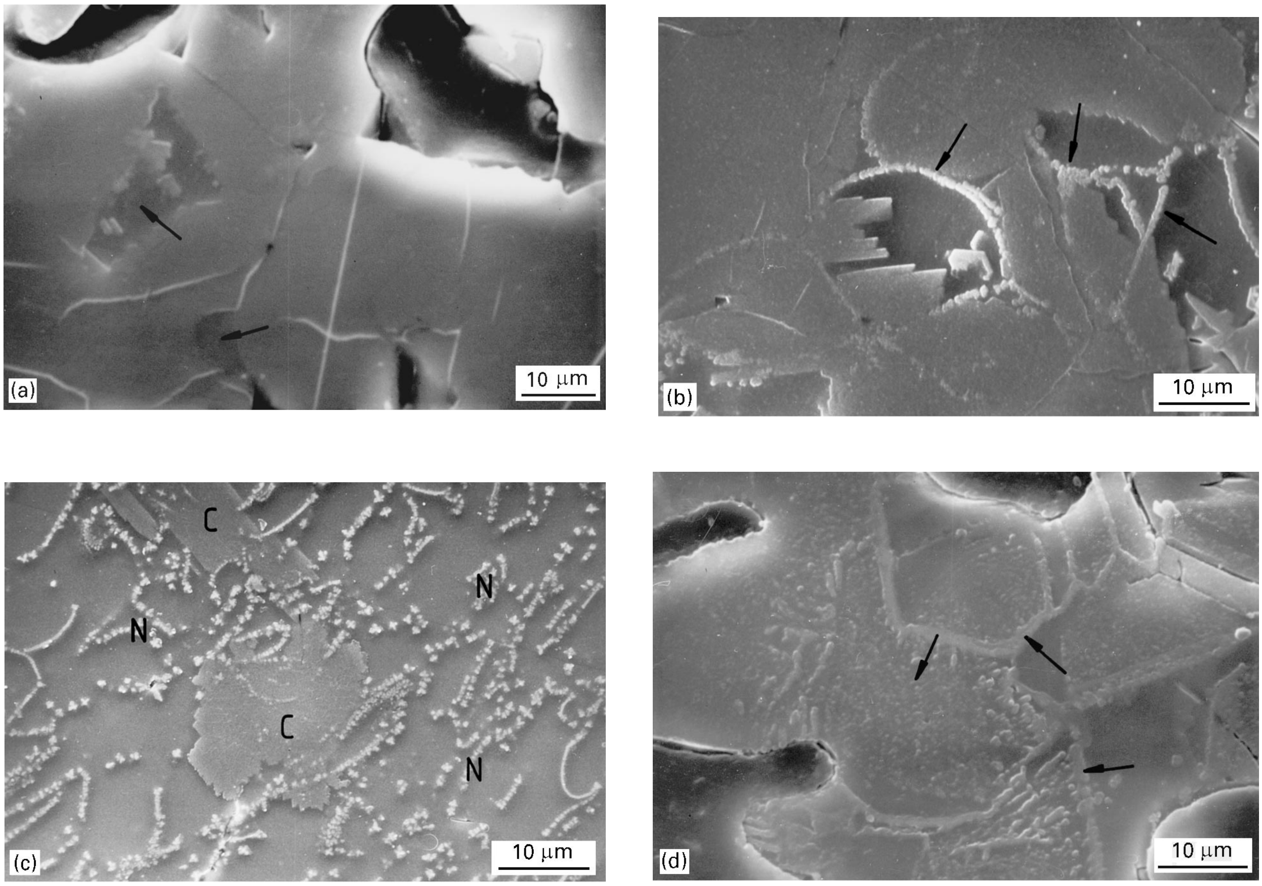

Figure 5 Microstructure of the volume-modified glass powders after heating up to 1100 °C at 10 °C min^{-1} (a) *S*10, (b) *S*20, (c) *S*40, (d) *S*80. For description of labels, see text.

between *S*0 and *S*100. The end temperature of the shrinkage remained constant for glasses *S*0–*S*10, it increased drastically by about 70 °C in glass *S*30 and decreased again by 120 °C between glass *S*60 and glass *S*100.

Fig. 5a–d gives an impression of the microstructure of the DTA samples, which have been heated up to 1100 °C at 10 °C min^{-1}. Glass *S*10 (Fig. 5a) was nearly completely crystallized to cordierite and showed only a few Na_2O-rich residual glass pockets (marked by arrows). The former glass grains were still identifiable and sintering was relatively poor. In glass *S*20 (Fig. 5b), the volume of residual glass became larger and nepheline began to crystallize heterogeneously on the cordierite surfaces forming strings of small crystals with a size of 0.5–1 μm (marked by arrows). With increasing Na_2O/MgO substitution, the amount of glass increased and that of cordierite (C) decreased, whereas the amount of nepheline (N) remained nearly constant at first (Fig. 5c). Only in the samples *S*80 and *S*100 did the amount of nepheline (marked by arrows) increase drastically and cordierite crystals were no longer detected (Fig. 5d). The amount of nepheline in samples *S*20–*S*60 and cordierite in samples *S*40–*S*60 was very low because they were not detected by means of DTA and XRD.

3.2. Surface modification

After the exchange process, the glass powders show a weight loss of 5%–10%. The aggressiveness of the salt melt seems to break up the glass network. Fig. 6 shows the diffusion profiles of Na^+ and Mg^{2+} in the glass grains as measured by means of EDX. Each data point represents the average of three measurements in different grains. It must be noted that the apparent measured concentrations do not necessarily correspond to the real concentrations, because the shape and thickness of the grain edges is not known and the

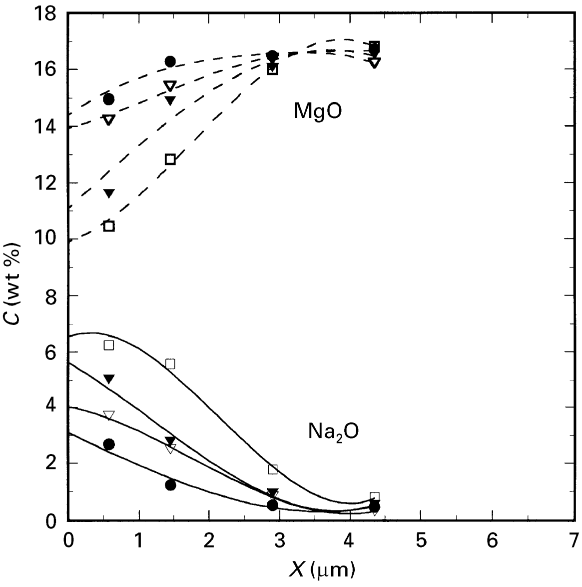

Figure 6 Concentration, *c*, of Na_2O and MgO as a function of the distance from the surface, *x*, and exchange time: (●) 2 h, (▽) 4 h, (▼) 6 h, (□) 8 h.

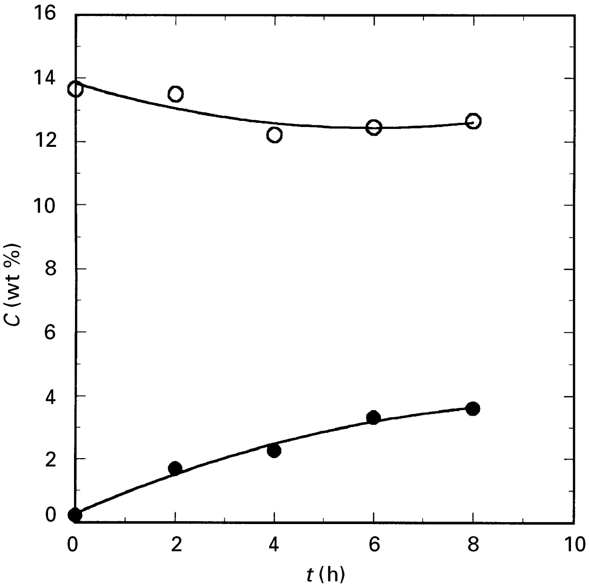

Figure 7 Bulk concentration, *c*, of (●) Na_2O and (○) MgO in the ion-exchanged samples as a function of exchange time.

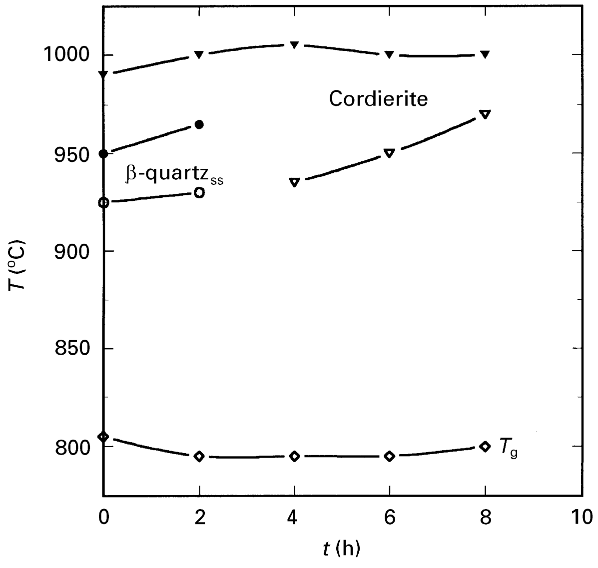

Figure 8 (▼, ●) DTA peak maxima of β-quartz$_{ss}$ and cordierite crystallization and (○, ▽, ◇) onset of crystallization as a function of ion-exchange time.

measured spots may overlap. The concentrations of SiO_2 and Al_2O_3 are always somewhat higher, respectively lower, at the edges than in the centre of the grains. The penetration depth of Na^+ exceeds not more than 3–4 μm at the applied conditions. With a penetration depth of 3 μm, the volume of the exchanged surface layer ranges from 66%–21% of the total volume, depending on the grain size range from 10–40 μm and assuming idealized spherical particles. The bulk concentrations of Na_2O and MgO in the exchanged glass powders as measured by AAS are shown in Fig. 7. The curves of the MgO decrease and the Na_2O increase are in accordance with the substitution $Mg^{2+} = 2Na^+$.

The DTA results are plotted in Fig. 8. The ion exchange has only a small influence on the overall T_g of the glass powder. In the unexchanged sample and the sample exchanged for 2 h, two crystallization peaks of β-quartz$_{SS}$ and cordierite can be distinguished. Above 2 h exchange time, only one cordierite crystallization peak was detected. Whereas the temperature of the peak maximum of the cordierite crystallization remains constant, the starting temperature of the crystallization increases with increasing exchange time from 925 °C to 970 °C. In all samples, cordierite was the only crystalline phase identified by means of XRD at the end of the crystallization process at 1000 °C.

Fig. 9 shows the sintering shrinkage of the exchanged glass powders. As expected, the shrinkage increases with increasing exchange time and reaches a maximum of nearly 14% in the sample exchanged for 8 h. Only the sample exchanged for 8 h was slightly deformed. The onset and the end of the sintering range is plotted in Fig. 10. The starting temperature decreases from 835 °C to 785 °C and the end temperature increases from 890 °C up to 910 °C with increasing exchange time. Thus the sintering range expands from 55 °C in the unmodified sample to 125 °C in the sample exchanged for 8 h.

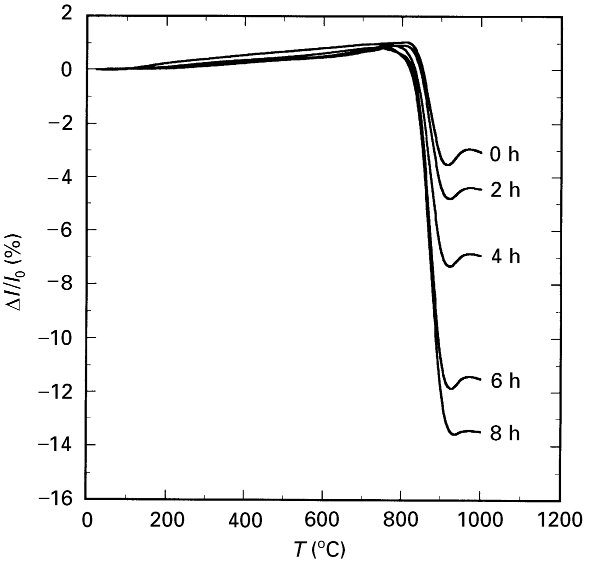

Figure 9 Sintering shrinkage $\Delta l/l_0$ of the surface-modified glass powders.

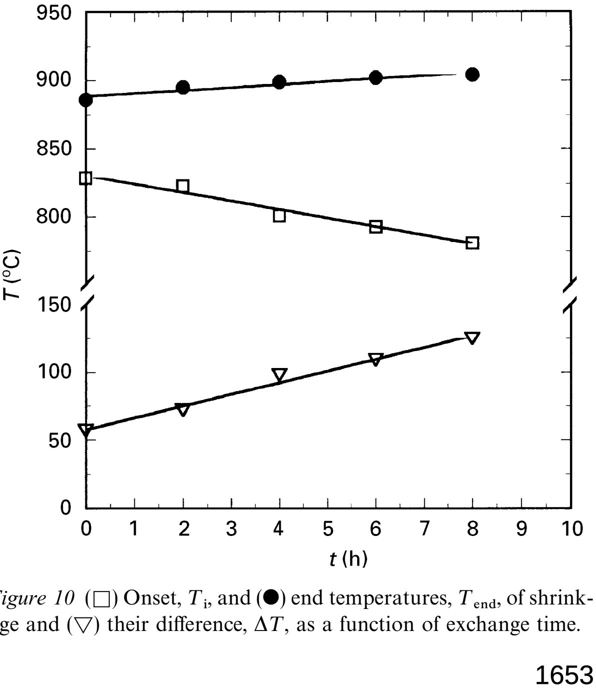

Figure 10 (□) Onset, T_i, and (●) end temperatures, T_{end}, of shrinkage and (▽) their difference, ΔT, as a function of exchange time.

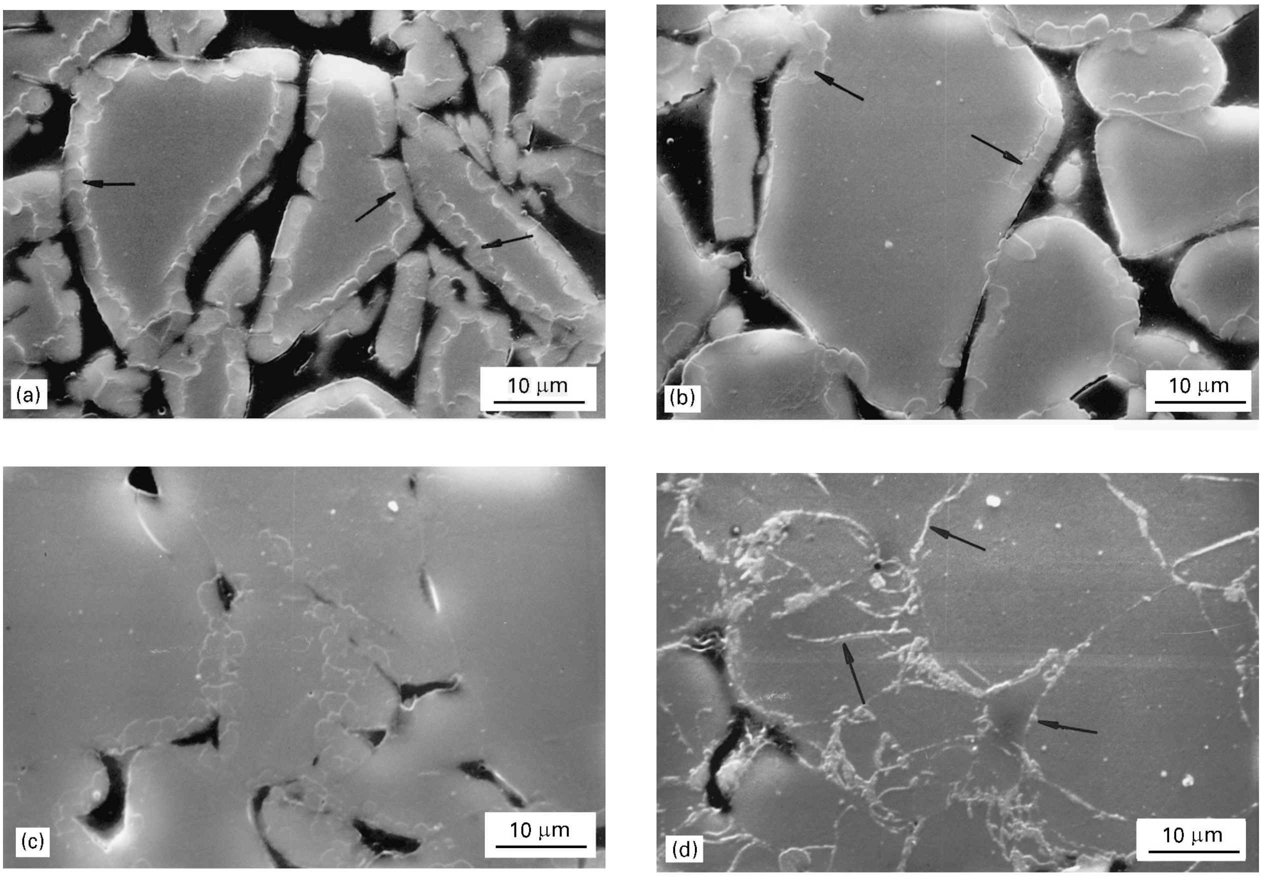

Figure 11 Microstructure of the surface-modified glass powders isothermally annealed for 10 min at 900 °C: (a) untreated, (b) exchanged for 2 h, (c) exchanged for 4 h, (d) exchanged for 8 h. For description of labels, see text.

The sequence of the changes in the crystallization behaviour and the microstructure of the modified glass powders annealed for 10 min at 900 °C is presented in Fig. 11a–d. The pure cordierite glass (Fig. 11a) shows strong surface crystallization of β-quartz$_{SS}$ (arrowed in Fig. 11a and b). The exchange of magnesium by sodium drastically decreases the amount of β-quartz$_{SS}$ crystals on the surfaces of the glass grains (Fig. 11b). With decreasing β-quartz$_{SS}$ crystallization the samples also show increasing sintering of individual glass grains (Fig. 11c). In the sample exchanged for 8 h (Fig. 11d) the sodium content is too high for the crystallization of β-quartz$_{SS}$ but allows growth of small nepheline crystals forming thin ribbons mostly along the former surfaces of the glass grains (arrowed).

4. Discussion

The experiments on the volume-exchanged glass powders demonstrate clearly that the temperature of the onset of the sintering range depends on the viscosity of the glass: the decreasing transformation temperature, T_g, which depends directly on the viscosity correlates with the decreasing temperature of the onset of the sintering.

The sodium ions are too large to be incorporated into the β-quartz$_{SS}$ structure, thus with increasing sodium content in the glass the amount of crystallizing β-quartz$_{SS}$ decreases and becomes zero at a substitution of 20%. It also seems difficult for the cordierite structure to incorporate sodium ions because the cordierite crystallization temperature increases and the amount of cordierite, determined from XRD, decreases with increasing sodium content. The crystallization data of β-quartz$_{SS}$ and cordierite from the DTA experiments correlate well with the end temperature of the sintering range up to *S*30: the crystallization of β-quartz$_{SS}$ ceases in glass *S*20 and the amount of crystallizing cordierite decreases resulting in a marked increase in the end temperature of the sintering range. In the surface-modified glass powder, these relations are somewhat different: although the T_g of the substituted glasses remains nearly constant, the starting temperature of the sintering range decreases with increasing substitution. This indicates that during the sintering process only the ion-exchanged surface layer of the glass grains is involved which has a lower viscosity. The overall viscosity of one glass grain is thus made up by a series of viscosities which increase continuously from the surface to the core, dependent on the Na_2O/MgO ratio.

The end temperature of the sintering range increases with exchange time in the surface-modified glasses due to the suppression of β-quartz$_{SS}$ crystallization. On the other hand in glasses of the *S* series with corresponding bulk composition (*S*0–*S*20) the end temperature of the sintering range remains constant with the exception of *S*20. The absolute temperatures are higher in the ion-exchanged glasses than in corresponding volume-exchanged glasses. In the former, the amount of crystallizing β-quartz$_{SS}$ decreases with increasing exchange time but the temperature and the amount of cordierite crystallization remain nearly constant. This is due to the unchanged composition in the centre of the glass grains. Consequently, sintering is halted through cordierite crystallization in the ion exchanged glasses, while in the volume-exchanged glasses, sintering stops due to β-quartz$_{SS}$ crystallization.

The presented experiments have shown that it may in fact, be sufficient to change only the chemical composition of the surface of the glass grains to improve their sintering behaviour. During the sintering process, only a surface layer is involved in the viscous flow of material into the pore regions while the cores of the glass grains seem to remain unaffected. The surfaces serve also as areas for nucleation and the first growth of β-quartz$_{SS}$ and cordierite which constitute the upper end of the sintering range. With the ion-exchange method a smaller amount of Na_2O is necessary to reach the same or better sintering and crystallization properties than with a bulk chemical modification. The amount of cordierite in the fully crystallized ceramic can be kept nearly as high as in the unexchanged sample. This is not possible with the conventional method of bulk chemical modification. However, there are a few points which have to be improved further to minimize the alkali content in the material and enhance sintering:

(i) at the conditions applied in this study, two processes compete with each other during the chemical treatment of the glass powder, the ion exchange of magnesium by sodium and the corrosion of the glass powder through the salt melt which results in a total weight loss of 5%–10%. In order to reduce the weight loss, it is necessary to alter the exchange conditions, i.e. salts utilized, time and temperature;

(ii) the ion exchange on a glass powder with a grain size range results in an inhomogeneous chemical distribution. Smaller grains have higher contents of sodium than larger ones because a larger ratio of their volume is exchanged. Locally high sodium concentrations also exist on bulging edges and protrusions. It is assumed that the sodium content can be further reduced when a glass powder with an homogeneous grain size and a more spherical shape is used;

(iii) a further improvement of the sintering can be obtained by reducing the grain size of the glass powder. This would also decrease the size of the flaws still existing in the studied sintered materials. However, it is essential to adjust the radius of the glass grains to the diffusion depth of the exchanging ions. When the grain size is reduced the diffusion depth must also be reduced in order to modify only a small surface volume of the powder. As sodium ions diffuse about 3–4 μm into the material at the applied conditions, it may be necessary to change to potassium or caesium ions which may show smaller diffusion depths due to their larger ionic radii.

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