OPEN-PORE GLASSES AND GLASS-CERAMICS
BY SINTERING OF MODIFIED PYROGENIC SILICIC ACIDS

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A pyrogenic silicic acid (Aerosil OX50) was used as glassy phase in salt sintering process. Aqueous disperoions of the Aerosil and β-tricalcium phosphate (TCP) particles, acting as spacers during the sintering process, were dried and sintered at temperatures in the range of 1000 °C to 1500 °C. After sintering, the crystalline spacer was leached by aqueous hydrochloric acid and highly porous glasses or glass ceramics were obtained. By dissolution of water-soluble salts of other ions (Na$^+$, Mg^{2+}, Al^{3+}...) in the aqueous dispersion, the pyrogenic silicic acid can be modified. The highly active surfaces of the SiO$_2$ particles are coated with the added compounds during drying the green compacts. The presence of sodium ions results in an enlargement of the silicatic network during sintering and the diffusion of these ions into the glassy phase is promoted. In this way, open pore glasses and glass ceramics possessing different chemical constitutions and pore diameters of 800 nm to around 15 μm were obtained. The total open porosity of the glasses can be varied by the amount of incorporated spacer TCP.

INTRODUCTION

In the past 50 years, the application of open-pore glasses and glass ceramics was extended to many fields in technology and medicine. Open-pore glasses work, for instance, as filter plates in industry and environmental technology. They are used for the immobilization of enzymes, bacteria and fungi in biotechnology and as carriers for functional layers or catalysts. In medicine, porous glasses are applied as materials for bone replacement. According to their application, they differ in chemical composition, porosity and pore diameter [1].

Porous glasses with pore diameters ranging from some millimetres to around 20 μm can be obtained by sintering techniques. However, conventional sintering shows some disadvantages: The production of open pores with a diameter of only a few micrometers is difficult, because such small pores can easily collapse caused by the viscous flow of the glasses during sintering. The total open porosity does not exceed 40 % to 45 % and the pore size distribution is wide. Therefore, a modified sintering process was developed [2, 3]. Before sintering, the glass powder is mixed with a salty phase possessing a defined grain size, a melting point above the sintering temperature of the glass and a high solubility in a solvent, in which the glass is insoluble. During the sintering process the salt acts as a spacer. After cooling, it is leached and in dependence on the glass to salt ratio, porous glasses with an open porosity of up to 75 % can be obtained. The diameters of the open pores depend on the grain size of the salt. Using this technique, also the pore size distribution can be controlled.

Porous glasses possessing pore diameters in the range of 0.5 nm to around 800 nm are usually produced by the VYCOR® (Corning Glass Works) process [4].

The principle is the selective leaching of an alkali--enriched borate phase of phase separated alkali borosilicate glasses. Extremely small pore diameters can also be obtained by the sol-gel-technique (mainly porous layers) [5]. However, there is a gap with respect to the pore size between porous glasses produced by phase separation techniques and porous glasses produced by sintering.

For glasses possessing a high open porosity, the strength is of great importance. Concerning open-porous glasses produced by the salt sintering process, it could be established, that the strength of the sintered materials is higher, if the grain size of the used glass powder is significantly smaller, than the grain size of the salt. The increased green density and the resulting short flowing paths of the glass during sintering may explain this behaviour. The described salt-sintering process is well suited to produce open pore glasses with pore diameters larger than 15 μm. However, the manufacturing of open pore glasses with smaller pores requires salt grain sizes of one micrometer or smaller and homogeneous glass powders with grain sizes of a few hundred nanometres or smaller. The production of such glass powders, for instance by milling, is very difficult, complicated and expensive. Therefore, a limit for the salt sintering process seems to be reached at pore sizes of around 10 to 15 μm.

In the following, investigations are described using modified pyrogenic silicic acids as glassy phase in the salt sintering process.

EXPERIMENTAL PART

The glassy component

Pyrogenic silicic acids are highly dispersed silicic acids produced by flame hydrolysis of tetrachlorosilane at very high temperatures (oxyhydrogen flame). The resulting glass particles possessing diameters between 10 nm and 100 nm are X-ray amorphous and they show thixotropic behaviour. Figure 1 gives the grain size distribution of the commercially available pyrogenic silicic acid 'Aerosil OX50' (Degussa AG, Germany) used in our investigations [6].
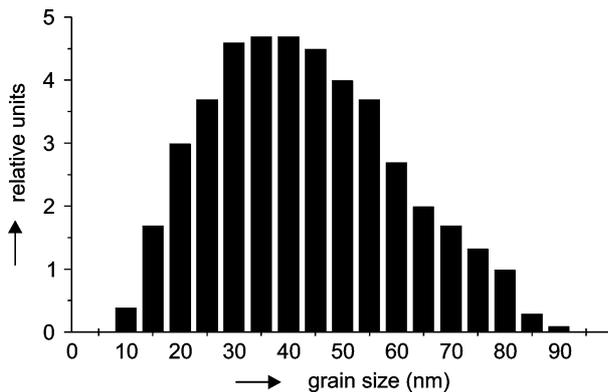

Figure 1. Grain size distribution of Aerosil OX 50.

Gentle drying of aqueous OX50-dispersions allows the production of crack free samples with a green density of 45 to 50 %. Investigations by Clasen [7] have shown, that the addition of small amounts fluoride promote the cross-linkage of the [SiO$_4$] units. An optimum of the sintering temperature was found at around 1500 °C.

The salt phase

The salt phase has to fulfil the following conditions: The melting point of the salt must be higher than the sintering temperature of the glassy phase. In this case, that means higher then 1500 °C. It must be insoluble in water, however, it must be soluble in acids, which do not attack the sintered Aerosil OX 50. There are only a few commercial salts possessing a melting point above 1500 °C as well as solubility in weak acid solutions. For the investigations described here, tricalcium phosphate (TCP) was selected. TCP has a melting point at 1730 °C and it is soluble in weak acids. TCP is decomposed by water as follows:

$$4\ Ca_3(PO_4)_2 + 2\ H_2O \leftrightarrow$$
$$\leftrightarrow Ca_{10}(PO_4)_6(OH)_2 + 2\ Ca^{2+} + 2\ HPO_4^{2-}$$
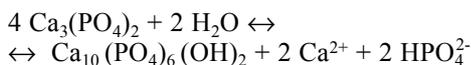
However, the reaction rate is low. Therefore, the dispersion of TCP in water is possible without significant decomposition. Small amounts of hydroxy-

apatite or monocalcium phosphate do not disturb. Corresponding to the phase diagram of the pseudo-binary system SiO$_2$-Ca$_3$(PO$_4$)$_2$ [8], no reaction should occur up to around 1550 °C.

Tricalcium phosphate was produced by the reaction of stoichiometric amounts of Ca(OH)$_2$ with aqueous H$_3$PO$_4$. The products were heat treated at 800 °C for three hours. The X-ray powder patterns showed only reflections of ß-TCP (JCPDS 9-169).

Modification of the glassy phase

In the further course of the investigations, it turned out that the pseudo-binary system Aerosil OX50 - TCP has some disadvantages, that requires the addition of Na$^+$-, Mg^{2+}- and Al^{3+}-ions. To guarantee a homogeneous "impregnating" of the Aerosil or the TCP grains only water-soluble salts of the ions were added. Besides sodium chloride, magnesium chloride hexahydrate and aluminium chloride hexahydrate were used.

Production of open pore glasses

In all cases, ammonium fluoride (1 % by weight) was dissolved in destilled water. To modify the glassy or the salt phase, the above mentioned sodium-, magnesium- or aluminium salts were additionally dissolved. Into these solutions, tricalcium phosphate (mostly 50 vol-% related to all other components) was given under stirring. During the following addition of the Aerosil, an increase in viscosity was observed and the dispersion was stabilized. Aerosil OX50 acts as a dispergator. Than, the dispersion was dried on a shaking machine at room temperature for one hour to support the desorption of bubbles and adsorbed air. The final drying was carried out in a furnace at temperatures between 40 and 100 °C for two days. Sintering temperatures between 1000 and 1520 °C were realized. After sintering, the TCP phase was leached by c HCl (mol l^{-1}) at 100 °C for one to three hours.

All probes were characterized by X-ray diffraction before and after leaching (D5000, Siemens, Germany). A scanning electron microscope DSM 940A (Zeiss, Germany) was used to investigate the porous glasses (glass ceramics).

RESULTS AND DISCUSSION

The pseudo-binary system SiO$_2$ (Aerosil OX 50) - TCP

Green compacts, produced by mixtures of Aerosil OX 50 and TCP in the above way described, were sintered at temperatures in the range of 1350 °C to 1520 °C. The samples were sintered to high density, however, they had many small cracks. As an effect of the sintering temperature, X-ray powder patterns of these samples showed the reflections of cristobalite and of α- and ß-TCP. Obviously, the observed cracks are the result of the phase transformation between high- and low- cristobalite at 272 °C coupled with a discontinuous

change of the thermal expansion coefficient ($\alpha_{20\text{-}300°C}$ = = 500×10^{-7} K^{-1}). Using Aerosil OX50 green compacts free of TCP, glassy bodies without cracks were obtained and the crystallization of cristobalite was only weak. The addition of TCP promotes the crystallization.

After leaching of TCP, open pore materials were obtained. However, the leaching acid was cloudy by fine-grained precipitates. After separation, the precipitates were identified as cristobalite by X-ray diffraction. Because of the insolubility of glassy SiO_2 and cristobalite in 1n HCl, the existence of cristobalite in the leaching liquid must be explained by interfacial reactions between the TCP-grains and the surrounding SiO_2 phase. Electron-beam micro analysis investigations have shown, that calcium and phosphate ions diffused into the surface of the formed silica glass (ceramic) matrix. The solubility of these areas is increased and a part of the small cristobalite crystals precipitates during leaching. This led to a loss of mechanical stability and the consistence of the resulting open pore materials was comparable with chalk.

The reaction between TCP grains and Aerosil can be lessened or avoided if the sintering temperature is decreased below 1300 °C. In these cases the reaction can be utilized to control the pore size.

Figure 2. shows the microsrtucture of a sample sintered at 1280 °C for three hours after leaching. The pore diameters range between 1 and 10 μm. The prolongation of the sintering time results in an intensified diffusion of calcium and phosphate ions into the SiO_2 matrix and the pore diameters are increased after leaching. Open pore materials produced by sintering below 1300 °C are mechanically stable. However, the crystallization of cristobalite cannot be avoided and the cracks caused by the phase transformation of cristobalite limit the application of these open pore materials to small dimensions.
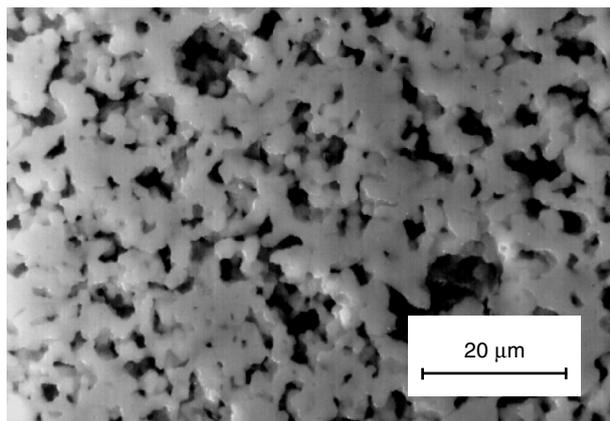

Figure 2. Scanning electron micrograph of a sintered glass ceramic after leaching.

The pseudo-ternary system SiO_2 (Aerosil OX50) - Na_2O - TCP

It is well known, that alkali ions stabilize the SiO_2 modification tridymite [9]. To avoid the crystallization of cristobalite described above, sodium ions in different amounts were added to the TCP free and to the TCP containing system. Table 1 gives the results of the sintering of the TCP free green compacts.

The addition of sodium ions results in a stabilization of the SiO_2-modification tridymite. It is surprising, that higher temperatures promote the crystallization of tridymite and lower temperatures the crystallization of cristobalite. Normally, it is reverse [9]. The required Na_2O amounts of 25 mol % or more decrease the viscosity and also a drastical decrease in the chemical stability has to be expected. The samples OX50Na10, OX50Na20 and OX50Na25 were in-

Table 1. Sintering of Aerosil OX50 / Na_2CO_3 - green compacts.

Probe	Added Na_2O	Sintering / crystal phases	
OX50Na10	9.7 mol.%	1000 °C / 3h	cristobalite, small quantities of tridymite
		1100 °C / 3h	cristobalite, small quantities of tridymite
		1200 °C / 3h	cristobalite, small quantities of tridymite
		1280 °C / 3h	cristobalite, tridymite
OX50Na20	19.5 mol%	1000 °C / 3h	cristobalite, tridymite
		1100 °C / 3h	cristobalite, tridymite
		1200 °C / 3h	cristobalite, tridymite
		1280 °C / 3h	tridymite exclusively
OX50Na25	24 mol.%	1000 °C / 3h	tridymite exclusively
		1100 °C / 3h	tridymite exclusively
		1200 °C / 3h	tridymite exclusively
		1280 °C / 3h	tridymite exclusively
OX50Na30	29.3 mol.%	1000 °C / 3h	glassy, molten
		1100 °C / 3h	glassy, molten
		1200 °C / 3h	glassy, molten
		1280 °C / 3h	glassy, molten

sufficiently sintered; they were brittle. Therefore, TCP (50 vol %) was added only to the sample OX50Na30.

After sintering, this sample is crystallized and the X-ray powder pattern showed the reflections of cristobalite, TCP and of a mixed sodium calcium orthophosphate phase possessing the stoichiometry $Na_3Ca_6(PO_4)_5$. The reflections of this phase increase with increasing temperature, while the reflections of TCP decrease. Favoured by the lowered viscosity, the sodium ions react with the TCP forming the mixed orthophosphate. Thus, a part of the sodium ions is fixed and the residual ions do not sufficiently stabilize tridymite.

The solubility of $Na_3Ca_6(PO_4)_5$ is equal or larger by comparison with that of TCP and the phosphatic phases can completely leached. However, the incorporation of sodium ions results in a break up of the silicate network and the solubility of the glass-(ceramic) matrix is strongly increased. After leaching the obtained open pore glass ceramics were brittle and partly destroyed.

The system SiO_2 (Aerosil OX50) - Na_2O - MgO - Al_2O_3 - TCP

To stabilize the TCP phase against the attacks of the sodium ions, MgO was added. The stabilizing effect of magnesium ions on tricalcium phosphate is known and was described by Dickens et al. in 1974 [10, 11].

Supplementary, aluminum ions were added, to increase the chemical stability of the material. The addition of magnesium and aluminum ions should also improve the glass formation. On this way, it should be possible to avoid the crystallization of cristobalite.

Figure 3 shows the X-ray diffraction powder pattern of a MgO- (18.1 mol.%) and Al_2O_3- (9.3 mol %) containing sample OX50Na30 possessing a TCP content of 50 vol.%. During sintering at 1200 °C for 3 hours, a crystalline whitlockite phase is formed by the reaction of the added magnesium ions and the ß-TCP.
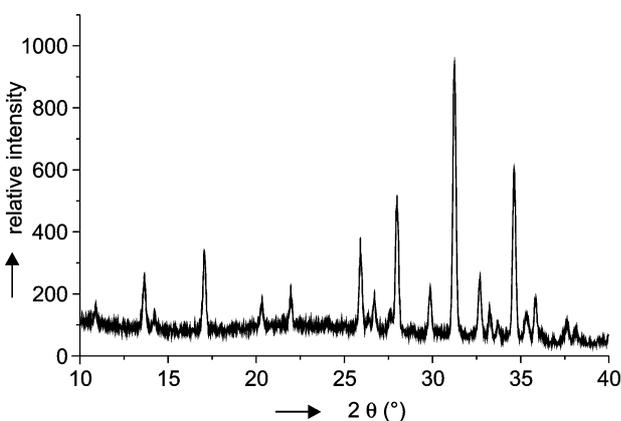
Figure 3. X-ray diffraction powder pattern of an Al_2O_3 and MgO containing probe OX50Na30 with 50 vol-% TCP after sintering at 1200 °C for 3 hours.

All X-ray reflections can be attributed to the crystalline phase $Ca_{18}Mg_2H_2(PO_4)_{14}$ (JCPDS 42-578). Normally, this phase is dehydrated at around 900 °C forming the dehydrated whitlockite phase $Ca_{18}Mg_2P_{14}O_{55}$ [12]. Probably, this phase was formed during sintering, however, no comparative powder patterns are available. The chemical stability of this magnesium containing phase is increased compared with that of ß-tricalcium phosphate. However, the prolongation of the leaching time in HCl ($c = 1$ mol l^{-1}) results in a complete dissolution of the whitlockite phase and in the formation of crack-free open pore materials.

Figure 4 presents a scanning electron micrograph of an Al_2O_3 and MgO containing sample after leaching in 1n hydrochloric acid for three hours. The magnesium containing whitlockite phase was dissolved quantitatively. In this case, the pore diameters range between 1 µm and 8 µm and the total open porosity amount to around 50 %. Both pore diameters and porosity can be varied using different quantities and different grain sizes of the TCP spacer. The walls between the pores are sintered to high density and were mechanically stable.
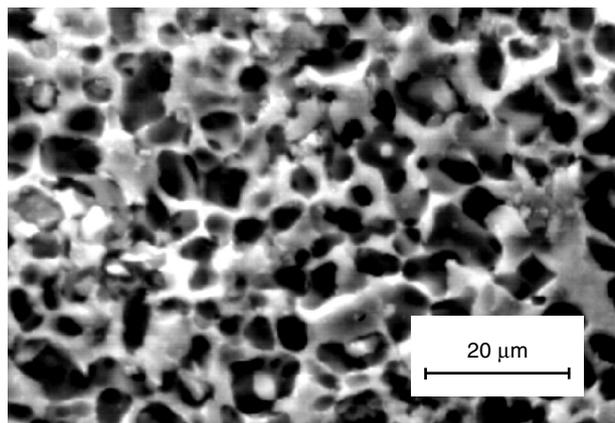
Figure 4. Scanning electron micrograph of a sintered Al_2O_3 and MgO containing probe OX50Na30 with 50 vol-% TCP after leaching.

CONCLUSIONS

Pyrogenic silicic acids are well suited as glassy phase in the salt sintering process. Because of the relatively high tendency to crystallization of the green compacts, a modification of the glassy phase by addition of suited ions (Mg^{2+}, Al^{3+}) is necessary. Tricalcium phosphate particles can act as spacers, if reactions between TCP and components of the glassy phase are avoided or compensated by incorporation of TCP stabilizing magnesium ions.

The modified salt sintering process described enables the preparation of open pore glasses possessing high total open porosities. Pore diameters between 800 nm and 15 µm were realized. In this way, it is possible to close the gap with respect to porosity between porous

glasses produced by phase separation techniques and porous glasses produced by sintering.

Acknowledgments

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SKLA A SKLOKERAMICKÉ MATERIÁLY PŘIPRAVENÉ SLINOVÁNÍM MODIFIKOVANÝCH PYROGENNÍCH KŘEMIČITÝCH KYSELIN

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Částice pyrogenní kyseliny křemičité (Aerosil 0X50) sloužily k vytvoření skelné fáze a částice β-fosforečnanu vápenatého (TCP) k vytvoření pórů v průběhu slinovacího procesu. Suspenze obou látek ve vodě byla vysušena a slinována v intervalu 1000 °C až 1500 °C. Po slinování byl TCP vyloužen vodným roztokem HCl. Získala se tak vysoce porézní skla nebo sklokeramika. Pyrogenní kyselinu křemičitou je možno modifikovat vodnými roztoky solí Na, Mg, Al, přidanými k suspenzi pyrogenní kyseliny křemičité. Vysoce aktivní povrch částic SiO_2 se pokryje přidanými sloučeninami během sušení suspenze. Přítomnost sodných iontů vyvolá zvětšení křemičité sítě během slinování a usnadní difuzi těchto iontů do skelné fáze. Uvedeným postupem se připravila porézní skla a sklokeramika s různým chemickým složením a s velikostí pórů od 800 nm do cca 15 μm. Celkovou otevřenou pórovitost skel je možno měnit v závislosti na obsahu vneseného TCP.