Original Paper

Open-pore sintered glass-ceramics as carrier material for biotechnological use[1)]

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Open-pore carriers with defined open porosity up to 45 % for biotechnological use were manufactured by sintering and crystallization of glass powders of cordierite stoichiometry. The stop of the shrinkage caused by a surface crystallization of the glass ("sinter blockade") is utilized to stabilize a desired pore volume without filler or foaming aids. Glass powders of the stoichiometric composition of cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) with different grain size distributions were used as starting materials. The efficiency of the sinter blockade and thereby the stabilized porosity of the resulting compact mainly depends on the surface nucleation density at the single glass particles which can be adjusted by powder processing. Furtheron, the chosen grain size distribution of the glass powders and the sintering process parameters (heating rate, temperature, heating time) are important factors to control the sintering behaviour.

Samples of carrier bodies produced by this way are tested and evaluated quantitatively as carriers for biofilms in a biotechnological process for decomposition of pollutants in a synthetic model waste water system.

Offenporige Sinterglaskeramik als Trägermaterial für biotechnologische Anwendungen

Offenporige Träger für biotechnologische Anwendungen mit definierter offener Porosität bis 45 % wurden durch Sinterung und Kristallisation von Glaspulvern der Stöchiometrie des Cordierits hergestellt. Die Beendigung des Sinterns wird durch eine Oberflächenkristallisation des Glases („Sinterblockade") bewirkt, wodurch die Stabilisierung eines gewünschten Porenvolumens möglich wird, ohne dabei Füllstoffe oder schaumbildende Hilfsmittel einsetzen zu müssen. Glaspulver der stöchiometrischen Zusammensetzung des Cordierits ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) mit unterschiedlichen Korngrößenverteilungen wurden als Ausgangsmaterial benutzt. Die Effektivität der Sinterblockade und das dadurch stabilisierte Porenvolumen der Sinterkörper sind hauptsächlich von der Oberflächenkeimdichte auf den einzelnen Glaspartikeln abhängig, die durch die Pulverherstellung und -behandlung eingestellt werden kann. Ferner sind die gewählte Korngrößenverteilung des Glaspulvers und die Sinterprozeßparameter (Heizrate, Temperatur und Zeit) wichtige Faktoren zur Kontrolle des Sinterverhaltens.

Proben von Trägerkörpern, die auf diese Weise hergestellt wurden, werden als Träger für Biofilme in einem biotechnologischen Prozeß zur Zersetzung von Verunreinigungen in einem synthetisch hergestellten Modellabwassersystem getestet und quantitativ bewertet.

1. Introduction

There is a trend to use more carriers in modern non-polluting biotechnology for immobilization of cells, bacteria, and enzymes at the carrier's surface. The use of carriers increases the efficiency of biotechnological processes: immobilized cultures do not have to be separated from the reactive solution or, as it would be possible without using carriers in the worst case, they are not lost together with the residual solution. Continuous biotechnological processing becomes possible by using carriers in reactors with a special adjusted and balanced flow rate of the reactive solution.

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Glass and ceramic materials are suitable carrier materials because of their favourable properties: high chemical durability, high mechanical strength (form stability), high temperature stability (which allows thermal regeneration and a repeated use), the possibility of non-polluting recycling, their good biocompatibility, and low costs of production. An open porous structure is desired for most applications of glass and ceramic carriers. This structure offers a large area for colonization of microorganisms including favourable pores for realizing their metabolism with components of the reactive solution.

The manufacture of glass or glass-ceramic porous carrier bodies can be based on the "glass particle sintering process" [1], the "Vycor process" [2], the "foam glass process" [3] or the "filler process" [4]. Compared to the conventional ceramic route, several advantages in the production of porous materials are brought about by the use of glasses: large temperature range for sintering, low sintering temperature, high purity of the starting materials and the final products, higher mechanical strength of materials with similar pore volume, simple powder processing. But there are two high-temperature steps necessary in producing porous carriers starting from glassy material (melting of the glass and sintering of glass particles), which may be estimated as disadvantage.

An alternative possibility stabilizing of the pore volume is the viscous sintering of glass powders combined with a carefully directed stop of the sintering process and shrinkage caused by crystallization (sinter blockade), which could be termed to be a "modified glass particle sintering process". This effect of negligible hindering from sintering up to a complete stop of the sintering process of glass particles occurs as regards glass powders of the stoichiometric composition of cordierite, and is started by a surface-nucleated crystallization process.

Shrinkage and crystallization (both determine the remaining pore volume) can be aimed at a special value by choosing the grain size of the glass powder, the sintering process (heating rate, temperature, heating time) and, in a very sensible way, by the surface nucleation density [5 and 6]. The surface nucleation density of the glass particles can be influenced to a useful number by the powder preparation route [7]. A production process using sinter blockade caused by crystallization does not need any additives, i.e., high purity of the final product can be realized. The production can be carried out in a non-polluting one-step thermal process, without use of acids or salts as in the "Vycor process" or the "filler process".

Aim of the investigations was to test the production range possibilities for carrier bodies using the sinter blockade process, to characterize the produced samples, and to test the application of the carrier bodies to the immobilization of biofilms used in a biotechnological waste-water-cleaning process.

In [8 to 10] it is reported about the successful use of cordierite ceramics for immobilization of mammalian cells for biotechnological production of pharmaceutics, including an excellent biocompatibility of this kind of carrier material, so that a promising application of open-pore cordierite glass-ceramic material to the immobilization of biofilms was supposed.

2. Experimental

2.1 Glass powder preparation

Glass batches of the stoichiometric composition (in wt%) of cordierite (13.7 MgO, 34.9 Al_2O_3, 51.4 SiO_2) were melted from pure raw materials (MgO, heavy, highest purity; γ-Al_2O_3, pure; amorphous SiO_2, pure) in a platinum/rhodium crucible at 1590 °C for 12 h. The glass melt was stirred for homogenization for 1 h, refined and then quenched in a water bath to produce a frit.

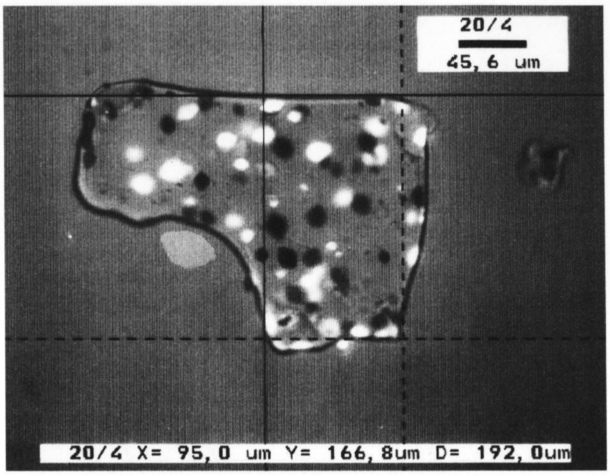

Figure 1. Micrograph of a single cordierite glass-ceramic grain under polarized light, showing a nucleation density of $2.0 \cdot 10^{-3}/\mu m^2$.

After drying in air at 120 °C for 48 h, the glass frit was crushed to a grain size <1 mm in a laboratory jaw breaker using tungsten carbide jaws and then crushed in a vibratory disc mill also using tungsten carbide as milling material, and the glass powder was sifted subsequently. It was possible by using this powder preparation route (breaking and milling procedure, milling time and milling material) to induce a surface nucleation density in the range between $2 \cdot 10^{-3}$ and $4 \cdot 10^{-3}/\mu m^2$. The determination of the nucleation density was performed microscopically under polarized light by counting the thermally developed (thermal treatment at 950 °C for 10 min) nuclei (small crystals) on the surface of single particles. Figure 1 shows a single cordierite glass-ceramic grain with a nucleation density of $2 \cdot 10^{-3}$ nuclei per square micrometre. It is possible to induce a surface nucleation density, carefully directed, in the range of four orders of magnitude (10^{-4} up to $10^{-1}/\mu m^2$) by choosing the breaking and milling procedure, milling time and milling material [7].

2.2 Manufacturing of open-pore glass-ceramic samples

For the production of open-pore sintered bodies different cordierite glass powder fractions were mixed with added binding agents and then pressed to green bodies with tablet shape (40 mm in diameter, 5 to 7 mm thickness) uniaxially, which were subsequently dried at 80 °C for 20 h (starting porosity of the samples 45 to 50 %) and then sintered in air under different thermal treatments (changing heating rate, temperature, heating time).

2.3 Examination of the sintered bodies

Open porosity (DIN 51056, method of measuring water capacity [11]), specific surface area (BET with krypton) and compressive strength (sample dimension: $(5 \times 5 \times 10)\ mm^3$) of the sintered samples were measured.

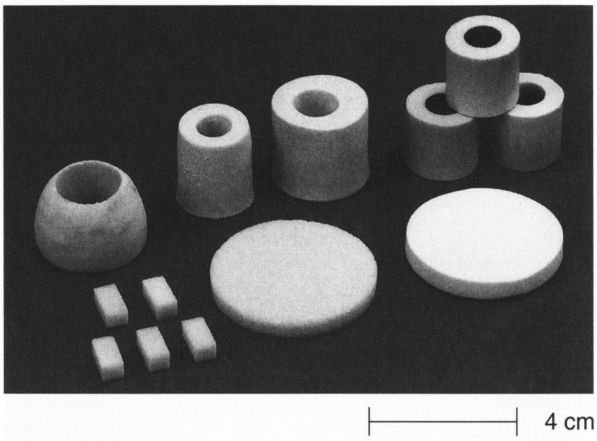

Figure 2. Different open-pore cordierite glass-ceramic bodies (laboratory-maufacturing).

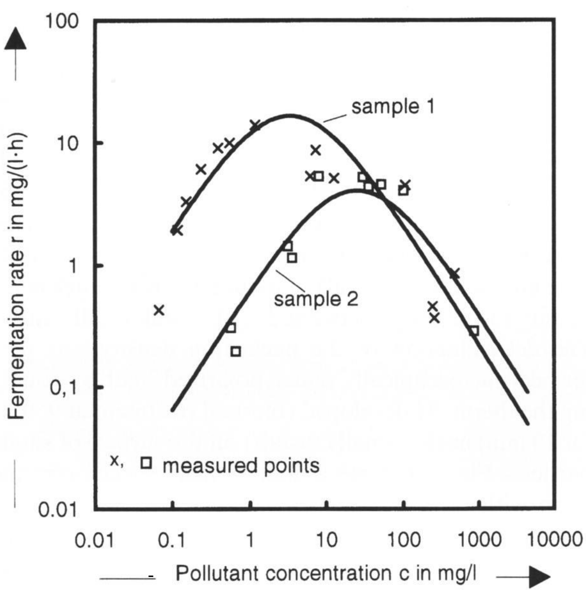

Figure 3. Fermentation rate as a function of the pollutant concentration and two open-pore cordierite glass-ceramic carrier charges measured under the same conditions as the biotechnological model decomposition process.

2.4 Manufacturing of carrier samples

After evaluation of the results for open porosity of the sintered samples, preparation routes for manufacturing of carrier bodies with the shape of hollow cylinders (similar to Raschig rings) and the desired porosity of 5, 10, 20, 25, 30 and 42 % open pore volume were deduced. Figure 2 shows different shapes of open-pore cordierite glass-ceramic bodies produced in the laboratory by using the sinter blockade method.

2.5 Application test of the carrier samples

The prepared bodies are tested in charges as carriers in a biotechnological process for decomposition of pollutants in an artifical model waste water system. They are used to immobilize microorganisms inside of a biofilm. The biotechnological process is carried out in a continuously working fermenter (1000 ml reactor volume, 100 sintered bodies per charge), a submerged fixed bed reactor (carrier bodies are completely dipped into the reactor solution), wherein p-nitrophenole ($C_6H_5O_3N$) as model pollution substance should be decomposed as follows:

$$C_6H_5O_3N \xrightarrow{O_2,\text{ microorganisms}} CO_2 + NO_2 + H_2O\,.$$

The aim of the biotechnological test is to optimize the biotechnological decomposition process and to adapt the results to the biodegradation of highly polluted, problematically degradable industrial waste water.

One parameter of biotechnological processing is (besides temperature, flow rate, microorganism population, concentration of pollutants and reactor construction) the quality of the carrier system. The evaluation of the suitability of the carrier bodies results from a comparison of the fermentation kinetics of the decomposition of the pollutant in the model waste water system. But this comparison is only possible if the fermentation rate of the different samples is measured under the same test conditions as function of the pollutant concentration. This is illustrated in figure 3 which shows the fermentation curves for two different open-pore samples. After finishing the still working experiments of biotechnological use of defined carrier sample charges, a quantitative method to characterize carrier biofilm systems should be deduced.

3. Results and discussion

As reported in [6], primary high-quartz solid solution crystals start to grow at 850 °C at the surface nucleation sites of cordierite glass particles, and stop viscous sintering at these sites (start of sinter blockade). At temperatures above 1000 °C the primary crystalline phase transforms quickly to the high-temperature modification α-cordierite.

The maximum value of open porosity of sintered materials produced by sinter blockade is 42 %.

Figure 4 shows, concerning an isothermal treatment, the influence of temperature and time on the open porosity of sintered bodies, prepared from powder fraction 63 to 125 µm.

Samples sintered at 850 °C only show a very small shrinkage, and the final state of sinter blockade cannot be achieved. On the other hand, at 1000 °C a nearly complete shrinkage occurs within 5 min, which, however, cannot go on to achieve bodies without pores because of very fast crystallization at that temperature. The curves mark an area of parameters, in which it is possible to set the final pore volume of sintered samples and to influence the pore diameter distribution (macropores) by choosing the sintering conditions for a special powder fraction showing a special surface nucleation density.

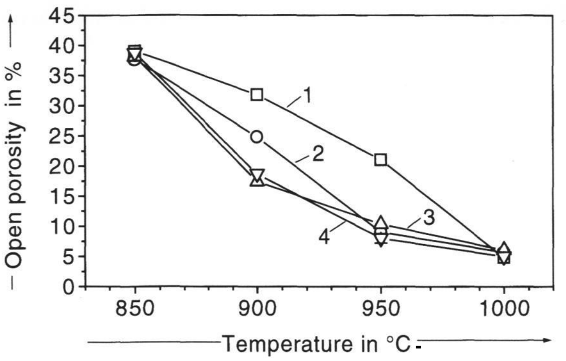

Figure 4. Influence of temperature and time, concerning an isothermal treatment, on the open porosity of sintered bodies, prepared from powder fraction 63 to 125 µm, nucleation density = $3.2 \cdot 10^{-3}/\mu m^2$. Curve 1: 5 min; curve 2: 30 min; curve 3: 60 min; curve 4: 120 min.

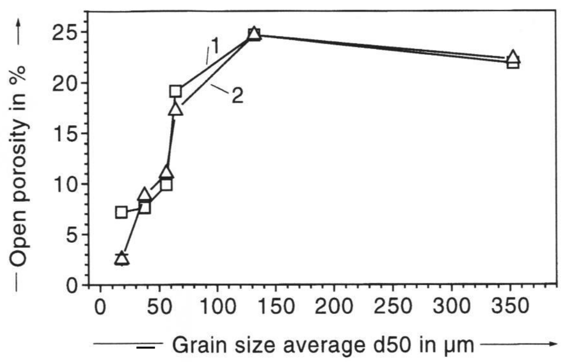

Figure 5. Relation of open porosity to the average grain size diameter d_{50} for two heating rates (curve 1: 5 K/min; curve 2: 20 K/min) up to 950 °C and 30 min heating time.

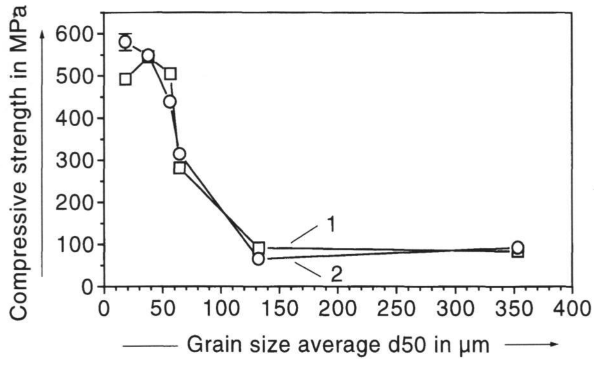

Figure 6. Relation of compressive strength to the average grain size diameter of the glass powder d_{50} for two heating rates (curve 1: 5 K/min; curve 2: 20 K/min) up to 950 °C and 30 min heating time.

Figure 5 shows an example for the relation of the open porosity of sintered bodies to the average grain size diameter of the glass powder d_{50}; the samples were sintered dynamically using two different heating rates (5 and 20 K/min) up to 950 °C and 30 min heating time.

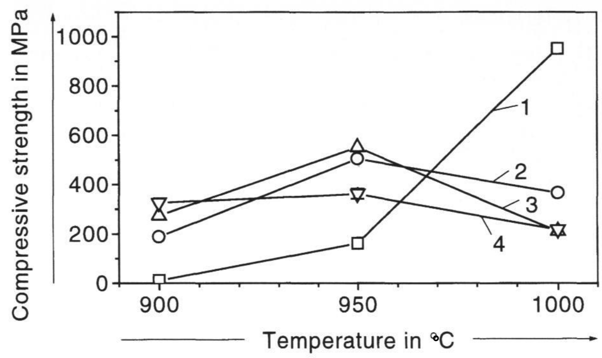

Figure 7. Compressive strength of sintered bodies of the powder fraction 63 to 125 µm in relation to sintering temperature and heating time for an isothermal process. Curve: 1: 5 min; curve 2: 30 min; curve 3: 60 min; curve 4: 120 min.

The values for the specific surface of the sintered bodies were found (BET measurement with krypton) in the range of 100 to 900 cm^2/g. The pore diameters are in the range of 4 to 100 µm (mercury high-pressure porosimetry).

As shown in figure 6, the compressive strength of the sintered bodies in relation to the average of grain size diameter of the glass powder d_{50} decreases with increasing open-pore volume, as expected (compare with figure 5). The values of compressive strength of the samples prepared by isothermal treatment of the fraction 63 to 125 µm were measured above 200 MPa for a wide range of porosity (figure 7). If low sintering temperatures are used, the compressive strength can be increased by longer heating time, caused by reducing the open-pore volume. This relation becomes reverse if higher sintering temperatures are used, i.e. after a short-time thermal treatment the resulting samples show a high compressive strength, but caused by a prolonged sintering process at that temperature a transformation of the primary crystalline phase (high-quartz solid solution crystals) to the secondary phase (α-cordierite) occurs, and this is accompanied by a decrease in the mechanical strength.

The results show that it is possible to produce open-pore sintered glass-ceramics with reproducible properties by stabilization of the pore system using a directed crystallization (sinter blockade) during the sintering process of a stoichiometric cordierite glass powder.

First results of testing the open-pore sintered bodies for carriers to immobilize biofilm systems in the above-mentioned fermenter for decomposition of the model pollutant p-nitrophenole show a significant increase in the decomposition rate, and an increase in the acceptable pollutant concentration in the waste water system in comparison with known carriers made of plastics, glass and hard porcelain.

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