

# Development of a gastight sealing material for ceramic components

N.H. Menzler\*, M. Bram, H.P. Buchkremer, D. Stöver

*Forschungszentrum Jülich, Institute for Materials and Processes in Energy Systems IWV-1, 52425 Jülich, Germany*

Received 1 August 2001; received in revised form 5 April 2002; accepted 11 April 2002

## Abstract

Within the framework of a cooperation project, ceramic components of alumina,  $\text{Al}_2\text{O}_3$ , were sealed in a gastight manner for chemical applications using a sealing compound based on ceramic raw materials. The sealing is adapted to the  $\text{Al}_2\text{O}_3$  ceramic with respect to expansion coefficient and wettability and it is inert, mechanically stable, chemically resistant and above all gastight at application temperatures of approx. 1000 °C. This was achieved with high reproducibility by a composition in the  $\text{SiO}_2$ – $\text{Al}_2\text{O}_3$ – $\text{CaO}$ – $\text{K}_2\text{O}$  quaternary system. The ceramic sealing compound is selectively crystallized by adequate temperature control and shows then the required high temperature resistance. The strengths achieved are sufficient for the planned application as a sealing material for a ceramic microreactor. The temperature cycling resistance and the thermal shock resistance are also adapted to  $\text{Al}_2\text{O}_3$ . Additional tests of commercial glass sealants were carried out to evaluate the results obtained. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:*  $\text{Al}_2\text{O}_3$ ; Joining; Sealing; Strength; Thermal shock resistance

## 1. Introduction

The properties of ceramic components with respect to temperature resistance, inertness, strength and in recent years also increasingly the possibility of miniaturization continuously open up new fields of application in the chemical industry, in microelectronics and as components in energy systems. For an application in the chemical industry a ceramic microreactor of alumina,  $\text{Al}_2\text{O}_3$ , was developed for the selective implementation of chemical reactions. One application is the oxidative, catalytically activated coupling of methane to ethylene. Moulding of the reactor casing (made by research centre Karlsruhe, Germany) and the installations was effected by means of a rapid prototyping technique, stereolithography and subsequent ceramic low-pressure injection moulding. Simultaneous moulding of the inlet and outlet tubes was found to be technologically impossible. Therefore these tubes must be sealed subsequently in a gastight manner. In addition to gastightness, further demands must be made on the sealing material such as an expansion coefficient adapted to the reactor material, mechanical stability, temperature cycling resistance,

thermal shock resistance, chemical inertness and low cost. The envisaged operating temperature of the reactor is approx. 1000 °C. Previous works on joining of alumina were carried out using a glass solder made of  $\text{SiO}_2$ – $\text{CaO}$ – $\text{Al}_2\text{O}_3$ ,<sup>1</sup> transient liquid phase layers,<sup>2</sup> alkaline-earth-metal-bearing bonding agents<sup>3</sup> or reaction sintering processes using zircon.<sup>4</sup> Ahn and Shiraishi<sup>1</sup> who used the glass solder were joining alumina parts at temperatures of 1500 °C for 20 min. The resulting connexion is mechanical stable, has an adequate coefficient of thermal expansion and is wetting well. Disadvantages of these systems are the use of high-purity chemicals and high soldering temperatures. The whole process is not optimised to cost-effective production. Locatelli et al.<sup>2</sup> used thin transient liquid phase layers for the bonding of oxide and non-oxide ceramics. For alumina they developed Cu/Ni/Cu and Au/Ni/Au interlayers with good mechanical strength and good wettability by incorporating Cr. Due to the chemical reaction taking place in the envisaged microreactor to be sealed metallic bonds could not be used due to their chemical non-inertness (including traditional active brazing with Ti). The joining of mullite with alkaline-earth-metal-bearing bonds was investigated by Sandhage et al.<sup>3</sup> The production route to produce strong bonds between the ceramic part and the bonding material requires flat,

\* Corresponding author.

*E-mail address:* n.h.menzler@fz-juelich.de (N.H. Menzler).

mostly parallel areas which were sealed by pressing the materials together and a subsequent heating step. This method could not be utilised for the sealing of the gas-conducting tubes to the microreactor because even the volume between the tube and the reactor must be sealed due to gas tightness. This cavity must be filled by a liquid sealant. Torrecilas et al.<sup>4</sup> used for the joining of mullite or alumina ceramics a reaction sintering process with zirkon. An ink is produced by dispersing the zirkon powder in ethyleneglycol. The sealing temperature needed for joining alumina to alumina is 1600 °C (1.5 h). Other sealing materials available are commercial glass sealants based on alkaline-earth aluminosilicates and semi-crystalline sealing compounds of raw materials from the ceramic industry prescribed partly by Hauth.<sup>5–7</sup> The composition of these sealing materials was optimized in the present work for the operating conditions described.

## 2. Ceramic microreactor

Manufacturing of the reactor casing by stereolithography and low-pressure injection moulding was described in earlier publications.<sup>8,9</sup> The present paper only briefly deals with the reactor design and its manufacturing. After moulding the reactor is provided with various installations, some of them with a complicated structure, such as catalyst support plates, sealing plates and gas channels for the educts and products (Fig. 1). These structural components were also manufactured by stereolithography and low-pressure injection moulding. For later operation of the reactor, the possibility of a replacement of the inner components is planned, e.g. for screening different catalyst materials or different gas channel structures. In contrast, non-separable gastight sealing to the reactor casing is planned for the inlet and outlet tubes. The tubes used consist of Al<sub>2</sub>O<sub>3</sub> material of the same composition as the reactor and are commercially available from Haldenwanger (W. Haldenwanger Technische Keramik GmbH & Co. KG, Berlin, Germany).

## 3. Experimental procedure

The sealing material serves for the gastight sealing of components made of alumina. The diameter difference between reactor case opening and tubes is approx. 100 µm so that a variable edge gap is obtained. Depending on the position and centering of the tubes, this gap is between 10 and 70 µm. For sealing, the sealing material is applied onto the ends of the tubes by brush, syringe or other application techniques and the tubes are then placed into the openings. It must be ensured that the sealing material adheres both in the edge gap and outside between tube and casing and does not run off.

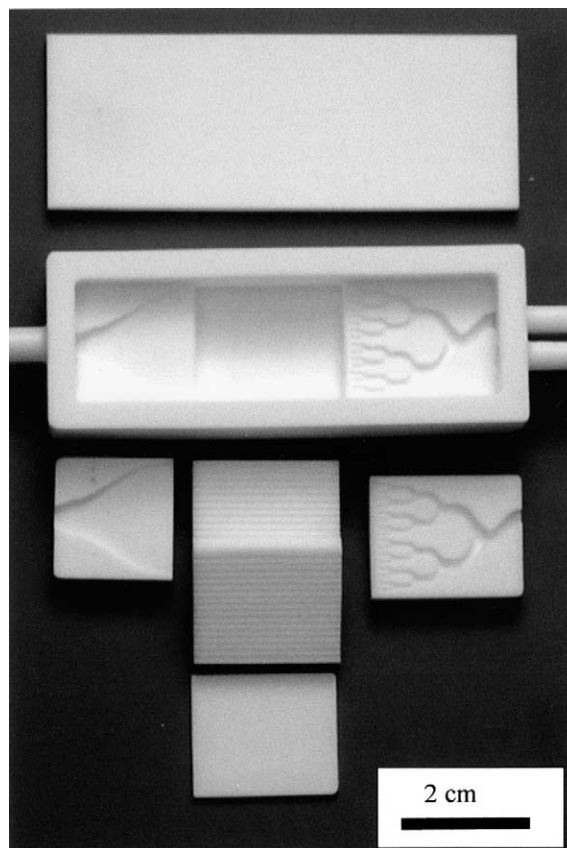


Fig. 1. Ceramic microreactor with installations (catalyst carrier, gas channels).

### 3.1. Sealing materials

#### 3.1.1. Glass sealings

Glass sealants of different quality are commercially available e.g. from Schott. There are basically three types of glass sealants: stable, crystallizing and composite glass sealants.<sup>10,11</sup> Stable, non-crystalline glass sealants can soften again during operation if they are reheated up to the processing temperature. They are thus ruled out for this application on account of their remeltability and, consequently, the insufficient stability of the sealing. The crystallizing glass sealants on offer have a maximum application temperature of 680 °C so that they are also ruled out. The only candidate glass sealant is an SiO<sub>2</sub>–MgO–CaO–BaO–Al<sub>2</sub>O<sub>3</sub> composite with a maximum application temperature of 1330 °C according to the manufacturer. The particle size distribution of the composite glass sealant (G018–105 from Schott, Germany) shows a *d*<sub>10</sub> of 2.5 µm a *d*<sub>50</sub> of 12 µm and a *d*<sub>90</sub> of 30 µm. A brushable and flowable paste is produced according to the manufacturer's specifications by adding a binder solution composed of 95 wt.% terpineol and 5 wt.% hydroxyethylcellulose (3.3 g added to 10 g of solid) to the glass sealant powder.

It has been found, however, that this mixture is not yet spreadable and thus not processable. Excess ethanol

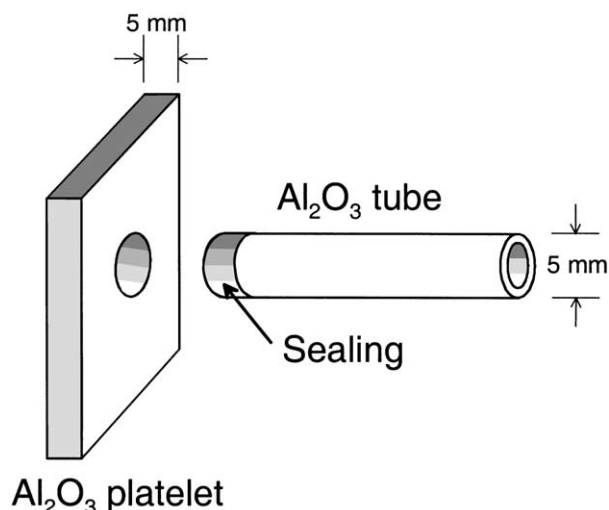


Fig. 2. Simplified geometry for sealing experiments.

was, therefore, admixed and subsequently evaporated until a spreadable material was obtained. This material was then used for preliminary experiments on a simplified specimen geometry (Fig. 2). This simplified specimen geometry consisted of an alumina platelet approx. 2 cm<sup>2</sup> in size, into which a hole with a diameter of 5.1 mm was drilled, and of tube segments made of Al<sub>2</sub>O<sub>3</sub> (5 mm diameter, approx. 30 mm length) that were lowered into these holes. It has been found that the processability of this powder can only be achieved by reducing the fine particle fraction in the glass sealant. When the fine particle fraction was too high, no wetting took place on the ceramic. This behaviour could be explained with the high amount of ethanol necessary to create a spreadable mixture with small particles and thus high particle surface. If the ethanol is evaporated during drying enhanced shrinkage occurs and therefore no layer-like wetting is obtained only wetted islands of particle agglomerations and regions with no sealant. Another explanation is an inhomogeneous melting behaviour. The finer particles of the material were melting at lower temperatures than the coarser ones and thus the melted phase migrates into the holes/pores

between the coarser particles and “glues” them together. Therefore separated agglomerates might be formed.

After the material had been applied, the specimens were dried in air and then sintered at temperatures of 1250–1350 °C. According to the manufacturer’s specifications, a sintering temperature of 1250 °C should be sufficient. This was not achieved. A homogeneously distributing sealing material was only obtained at a temperature of 1300 °C. Only with this adapted temperature programme was it possible to seal the tubes gastight onto the platelet. The results of the preliminary experiments were also transferable to the reactor with the associated tubes. However, after ordering a new batch of the glass sealant powder it was found that it was not possible to reproduce the sealing process despite identical experimental parameters. For this reason, no further tests were carried out using composite glass sealants.

### 3.1.2. Ceramic sealing material

In parallel with the experiments with glass sealant, tests were carried out with sealing compounds made of ceramic raw materials. These compositions are based on the results obtained by Hauth<sup>5–7</sup> and have been further developed for the present application using mixtures of potassium feldspar, quartz, kaolin, wollastonite, nephelinsyenite and bentonite. The average particle size, the linear coefficient of thermal expansion and the raw material suppliers are listed in Table 1. Fig. 3 shows the particle size distributions of the raw materials used. The raw materials have relatively wide, but similar distribution functions (between 1 and 100 μm). The *d*<sub>50</sub> values vary between 4 and 30 μm. Table 2 shows the chemical composition of the raw materials. The essential constituents are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, alkaline earths and alkalis.

**3.1.2.1. Sample preparation.** First of all, two standard compositions for applications up to 1500 °C (sample “A”) and up to 1300 °C (sample “B”) were prepared (Table 3) based on the data of Hauth.<sup>5</sup> Both were obtained by melting according to the literature. In order

Table 1  
Physical parameters of ceramic raw materials

Raw material	Average particle size <i>d</i> <sub>50</sub> (μm)	Linear coefficient of thermal expansion $\alpha$ ( $\times 10^{-6} \text{ K}^{-1}$ )	Supplier
Potassium feldspar	21.27	$\sim 10.8^{16}$	AKW, Amberger Kaolinwerke
Quartz	29.91	0.5–0.9	AKW, Amberger Kaolinwerke
Kaolin Meka	3.70	4.2–4.6 (50–700 °C)	AKW, Amberger Kaolinwerke
Kaolin Oka	3.94	4.2–4.6 (50–700 °C)	AKW, Amberger Kaolinwerke
Wollastonite	14.19	6.0 (20–300 °C)	Quarzwerte Frechen
Bentonite	17.48	–	Süd-Chemie AG
Nephelinsyenite	21.38	6.5 (20–300 °C)	Quarzwerte Frechen

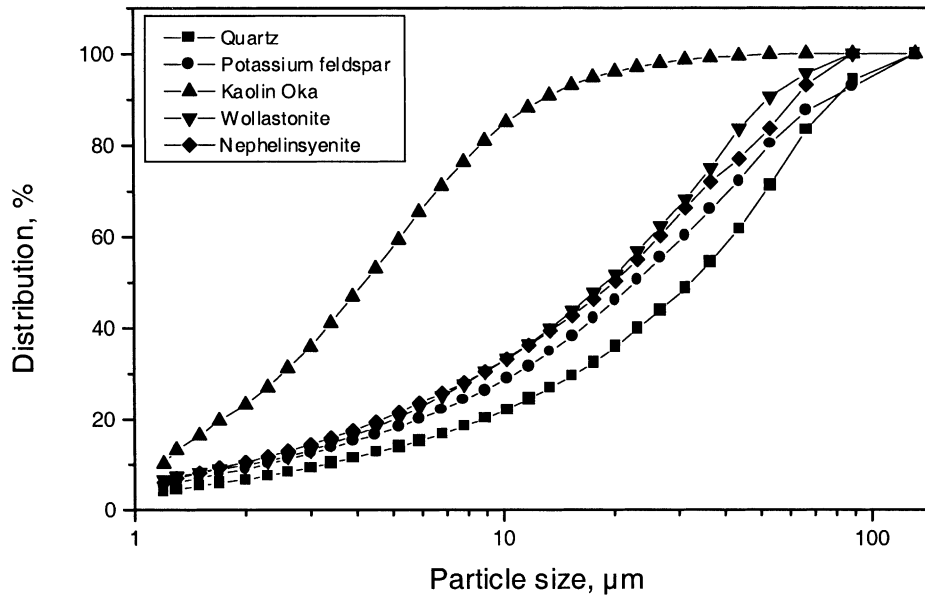


Fig. 3. Particle size distribution of ceramic raw materials.

Table 2  
Chemical composition of ceramic raw materials (wt.%)

Oxide	Quartz	Potassium feldspar	Wollastonite	Kaolin Oka	Nephelinsyenite	Bentonite
SiO <sub>2</sub>	98.7	65.8	50	52.5	60.8	48.3
Al <sub>2</sub> O <sub>3</sub>	0.6	17.8	1	33.8	23	16.2
Na <sub>2</sub> O	0.00	0.8	0.2	0.01	10.4	4.2
K <sub>2</sub> O	0.30	14.65	–	0.26	4.6	1.8
CaO	0.02	0.04	45	0.17	0.05	6.6
MgO	0.03	0.02	0.8	0.20	0.03	3.5
Fe <sub>2</sub> O <sub>3</sub>	0.03	0.04	0.3	0.37	0.08	5.7
TiO <sub>2</sub>	0.05	0.04	–	0.15	–	0.3
Ignition loss	0.2	0.2	3	12.5	0.7	12.6

to achieve a higher mechanical strength of the sealing, it was attempted to selectively crystallize mineral phases such as wollastonite or mullite in the sealing compound. Increased mechanical stability is necessary because reactor operation will be at overpressure so that pressure is also exerted on the sealed connection. In order to prevent the tubes from being pressed out of the reactor casing, it is therefore necessary to obtain a more intimate connection. In order to achieve crystallization, the composition and sintering programme parameters can be varied. First of all, a batch with a reduced mixing water content was prepared in order to find out whether the material still remains processable in this composition (sample “C”). Samples “D1”–“D4” represent the variation of the composition for selective crystallization. Initial experiments (sample “B”) showed that crystallites are already produced during normal sintering. However, they only occur very irregularly. The only crystalline phase identified by XRD was wollastonite,

Ca<sub>3</sub>[Si<sub>3</sub>O<sub>9</sub>]. Crystallization of mullite should be aimed at since its mechanical properties are better than those of wollastonite. The reason for the crystallization of wollastonite instead of mullite could be the small fraction of Al<sub>2</sub>O<sub>3</sub> in the base material. Mullite, Al[AlSiO<sub>5</sub>], consists in its ideal composition of 63% Al<sub>2</sub>O<sub>3</sub> and 37% SiO<sub>2</sub>. The Al<sub>2</sub>O<sub>3</sub> concentration in potassium feldspar is only 18% and the total alumina content in sealing compound “A” is 12.6%. For this reason, the Al<sub>2</sub>O<sub>3</sub> fraction in the compound was increased by successively replacing the potassium feldspar by nephelinsyenite (Al<sub>2</sub>O<sub>3</sub> content 23%). For this purpose, a mixing series beginning with 34% feldspar/16% nephelinsyenite (sample “D1”) through 25/25% (sample “D2”), 16/34% (sample “D3”) up to 0% feldspar and 50% nephelinsyenite (sample “D4”) total Al<sub>2</sub>O<sub>3</sub> content 15.2%) was molten with always the same sintering programme.

The variation of the sintering regime was studied using samples “A”, “B” and “G” (Table 3; note that the

Table 3  
Variation of composition of sealant

Batch	Feldspar (wt.%)	Quartz (wt.%)	Wollastonite (wt.%)	Kaolin (wt.%)	Nephelinsyenite (wt.%)	Bentonite (wt.%)	Water (ml per 100 g solid)
A	50	10	30	10	–	–	70
B	89	–	–	10	–	1	60
C	50	10	30	10	–	–	50
D1	34	10	30	10	16	–	70
D2	25	10	30	10	25	–	70
D3	16	10	30	10	34	–	70
D4	0	10	30	10	50	–	70
E	16	10	30	10	34	–	70 <sup>a</sup>
F	16	10	30	10	34	–	70 <sup>b</sup>
G	16	10	30	10	34	–	70 <sup>c</sup>

<sup>a</sup> With 0.1 wt.% (per solid) stabilizer.

<sup>b</sup> With 0.3 wt.% (per solid) binder and 0.6 wt.% (per solid) dispersant.

<sup>c</sup> Variation of sintering parameters.

composition of “G” is comparable to “D3”). The standard sintering programme of sample “A” is:

RT → 400 °C, 5 K/min, 30 min holding time  
400 → 1300 °C, 5 K/min, 180 min holding time  
1300 °C → RT, 5 K/min.

The sintering regime for sample “B” differs from that of sample “A” only in a higher melting temperature of 1400–1500 °C.

After various sintering experiments without achieving the crystallization of mullite, an optimum sintering programme was found for sample “G” achieving the crystallization of wollastonite:

RT → 1300 °C, 5 K/min, 180 min holding time  
1300 → 1000 °C, 5 K/min, 180 min holding time  
1000 °C → RT, 5 K/min.

The holding time at  $T_{\max}$  serves here to completely melt all raw materials and the holding time at 1000 °C serves to crystallize the wollastonite. At a reactor operating temperature of 1000 °C, crystallization will proceed in the application case until all the oxides necessary for mineralization from the amorphous phase are consumed.

For better adhesion of the sealant to the reactor walls after applying, commercially available additives were admixed to the raw material mixture. Sample “F” contains, for example, 0.3% binder and 0.6% liquefier (relative to the solid content).

The gastightness of finish-sealed reactors was tested at Research Centre Karlsruhe at room temperature and 1000 °C. At RT, the gastightness is tested under water (bubble test). For the tests at 1000 °C, the mid-section of the reactor is heated up by means of resistance heating and the amount of air supplied and discharged before and behind the reactor is determined with the aid of flow meters.

The crystalline phases produced were characterized by means of X-ray diffractometry and light microscopy. Two tests were carried out to investigate the thermal properties: a cycling test from RT to 1000 °C and back to RT (10-fold) and a thermal shock test by rapidly cooling a sample from 1000 °C in a water bath. The mechanical stability of the sealed connection was examined *in triplicate* by a 4-point bending test with Al<sub>2</sub>O<sub>3</sub> rods of the dimensions 2.5×4×50 mm<sup>3</sup> (testing machine of the INSTRON 1362 type; span length upper rolls 20 mm, lower rolls 40 mm). For this purpose, the rods were sawn up in the middle, ground with parallel faces and then provided with sealing material on the ends. Subsequently, the two sawn-up specimen parts were sealed, dried and sintered. After cooling down, all four faces were ground once more to remove any adhering sealing material. The test parameters of the bending test are: temperature 1000 °C, heating rate 8 K/min, power-controlled speed 200 N/min.

Finally, the inertness of the sealed connection was examined by 12-h storage in 40% hydrofluoric acid.

## 4. Results

### 4.1. Glass sealings

The commercially available composite glass sealant was found to be unsuitable for an industrial-scale application of the compact reactor due to the batch-dependent processing parameters of the sealant for connecting tubes and casing.

### 4.2. Ceramic sealing material

#### 4.2.1. Variation of composition

Using the example of samples “D1”–“D4”, Fig. 4 shows that the crystallization of the sealing starts at the

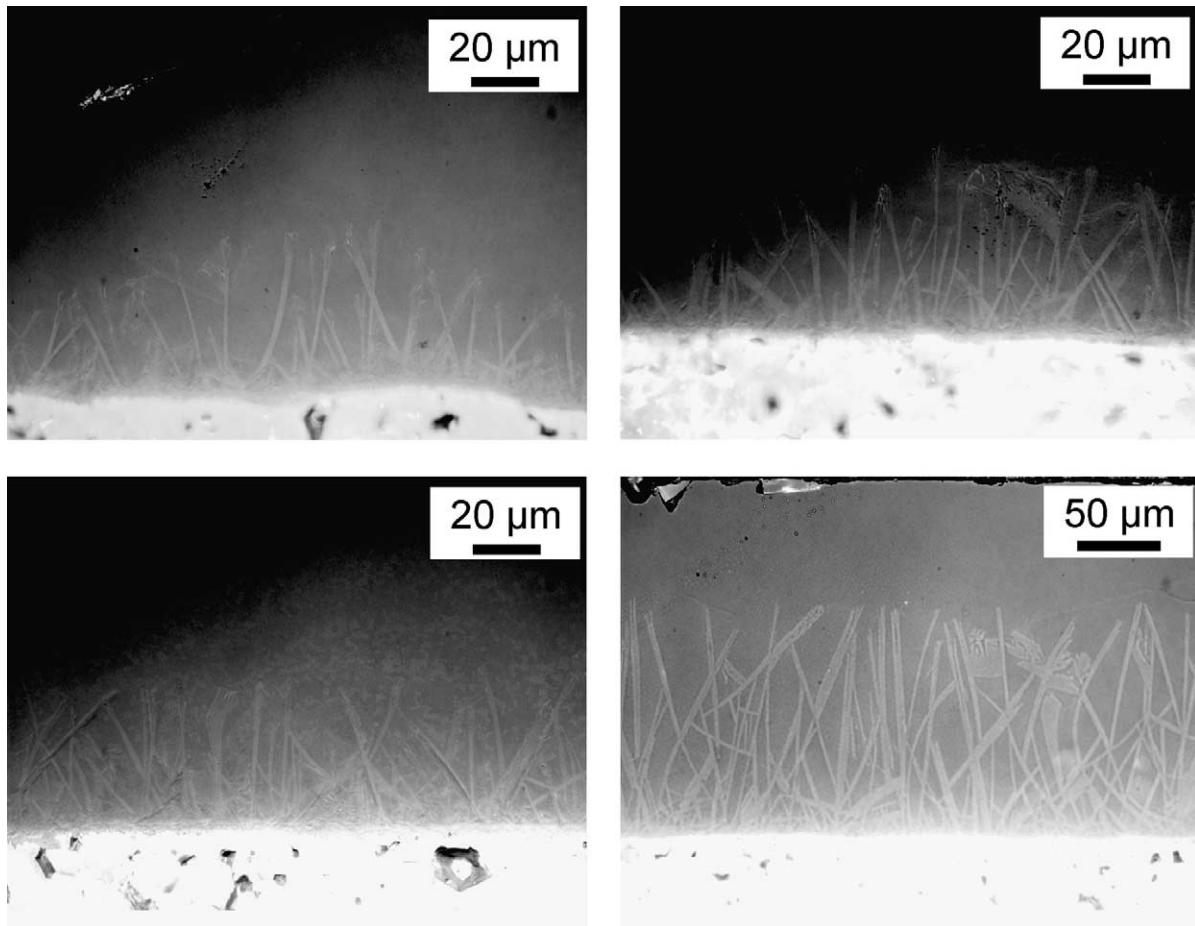


Fig. 4. Light microscopy of samples D1 to D4 (top left: D1; top right: D2; bottom left: D3; bottom right: D4); influence of sintering parameters on crystallization behaviour of the sealing material.

$\text{Al}_2\text{O}_3$ /sealing material interface. From there, acicular crystals grow into the amorphous matrix. The crystal length/crystal width ratio increases with increasing nephelinsyenite content and subsequently replacing the content of potassium feldspar. Moreover, the number of crystallites also increases. Hence follows that the use of nephelinsyenite instead of potassium feldspar enhances crystallization under identical sintering conditions. XRD measurements show that the crystallized phase is wollastonite too. In contrast, after prolonged holding time, the wollastonite in standard sample “A” essentially crystallizes in the matrix itself (Fig. 5). The different crystallisation behaviour may be described as follows: through substitution of faldspar by nepheline not only the amount of alumina in the composition increases but additionally the alkali ratio between sodium and potassium is moved to the sodium side. Trough increasing the amount of sodium the viscosity of the melt is increased due to the fact that sodium acts more than potassium as reducing agent because of its ionic size. The fact that the bulk crystallization starts only if feldspar is removed totally by nepheline and not slowly enhanced by the raw materials change could be

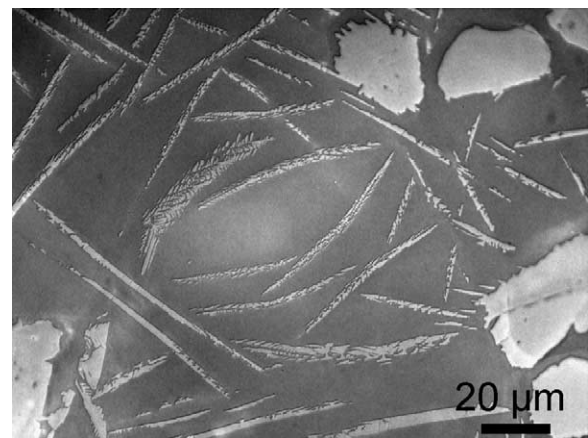


Fig. 5. Light microscopy of sample A; wollastonite crystals after increasing holding time.

declared thereby that in a mixed alkali system the sluggish component dominates the reaction. In this case potassium is the slowest reaction partner and thus only if the potassium is reduced totally the sodium can enhance the reaction. The reaction which is enhanced through sodium is the increasing of the nuclei formation

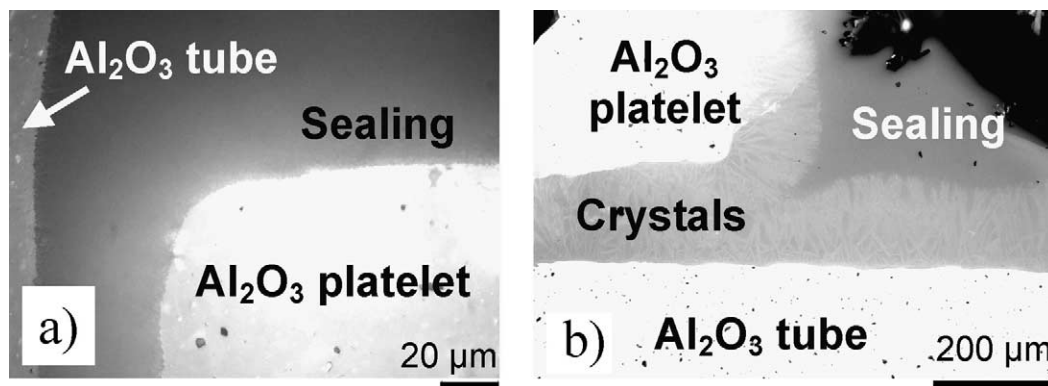


Fig. 6. Light microscopy of samples A a) and D4 b); comparison of different crystallization behaviour.

probability by enhancing of the viscosity (more rapid diffusion) and decreasing the crystal activation energy. The difference in crystallization becomes particularly evident in a comparison of samples “A” and “D4” (Fig. 6a and b) showing the edge gap zone between base plate and outer tube wall. Whereas in the case of sample “A” no mineral phases can be recognized in the gap between reactor casing and alumina tube that is completely filled with sealing material, this zone is characterized in sample “D4” by homogeneous crystallization across the entire gap cross-section. The influence of this different crystallization and of the greater crystalline phase fraction in sample “D4” becomes apparent when measuring the strength of the sealed connection. The 4-point bending strength of standard sample “A” at room temperature is of the order of the alumina base material since the test rods do not break in the sealing but in the base material. This also applies to sample “D4”.

A different picture is obtained by a high-temperature strength measurement at 1000 °C, where a test rod of the “A” composition already bends at 900 °C under a preload of 2 N due to softening of the amorphous phase, so that a measurement at 1000 °C is no longer possible. For this reason, a sealing material of the “A” composition cannot be used at the envisaged operating temperature of 1000 °C. In comparison to the standard sample, it was also possible for sample “D4” to determine strengths at 1000 °C. The strength values of 4-point bending ranged between 82 and 123 MPa. The associated Young’s moduli of sample “D4” range from 207 to 227 GPa (at 1000 °C). The great scattering of the strength values of the samples (measurement at three test rods,  $\sigma = 5\text{--}20\%$ ) may be caused by the sealing technique of the bending test rods. The two parts of the rods were sealed without additional force prior to the test after brush application of the sealing compound. The experiments show that the required high temperature resistance and strength are only achieved by selectively enhancing the degree of crystallization of the sealing compound. A comparison of the strengths and Young’s

moduli in sealing with high-purity alumina provides values of 280–330 MPa for the strength and 280–380 GPa for Young’s modulus<sup>12</sup> (4-point bending). This means that the strength values of the sealing compound at 1000 °C are below those of the material to be sealed by a factor of 2–3.

The aim of the crystallization of mullite in the sealing compound has neither been achieved by varying the composition nor by adapting the sintering programme. As an explanation the comparison to traditional porcelain may be useful. The classic porcelain composition is 50 wt.% kaolinite, 25 wt.% feldspar and 25 wt.% quartz.<sup>13</sup> By neglecting the minor components like calcium, magnesia, iron oxide and sodium oxide the major oxides are those of silicon, aluminum and potassium. A classical composition is thus: 72 wt.% SiO<sub>2</sub>, 24 wt.% Al<sub>2</sub>O<sub>3</sub> and 4 wt.% K<sub>2</sub>O (underlying the raw materials used in this work) which means a SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> ratio of 3. In the presented composition this ratio is between 6 and 7 and therefore the amount of alumina is too small for the formation of mullite. While the used crystallisation temperature of 1000 °C should be appropriate for mullite formation.<sup>14</sup> It may thus be concluded that the selective formation of mullite can only be achieved by adding mullite nuclei. Candidate materials are, for example, kaolin fireclays which is commercially available and already contains a mullite fraction of approx. 45%.

#### 4.2.2. Variation of sintering regime

It can be seen from Figs. 5, sample “A” and 7, sample “D4” that, in addition to varying the holding time at  $T_{\max} = 1300$  °C, above all a second holding time at lower temperatures (900–1100 °C) can be used for selective crystallization. Fig. 5 shows crystallization under standard conditions, i.e. a holding time of 180 min at 1300 °C. A few isolated crystallites are obtained with a maximum length of approx. 10 µm in the matrix material. An extension of the holding time to 300 min does not show any influence on crystallization behaviour. Only

the introduction of a second holding time after maximum temperature in the range of 900–1100 °C and a holding time of 180 min leads to a clear extension of the crystallites (190 µm) and above all to a denser crystal structure (Fig. 7).

Sample “B”, which clearly differs in its composition (bentonite, see Table 2) from the other samples and which must be sintered at  $\geq 1400$  °C, exclusively shows amorphous regions after sintering. No crystallization takes place here even under varying sintering conditions.

The reproducibility of the experiments was high so that processability and sinterability with selective crystallization were given even in the case of slight variations of the composition of the natural raw materials.

#### 4.2.3. Thermal and chemical behaviour

In addition to the influence of composition and sintering regime on the crystallization behaviour of the sealing compound, its thermal, chemical and mechanical behaviour was examined. The linear coefficient of thermal expansion (20–400 °C) of the samples, calculated

according to Appen<sup>15</sup> on the assumption of a pure glassy matrix (without crystallites or inclusions), varies between  $7.0 \times 10^{-6} \text{ K}^{-1}$  (sample “A”) and  $7.3 \times 10^{-6} \text{ K}^{-1}$  (sample “B”). Due to the successive replacement of feldspar by nephelinsyenite in samples “D1”–“D4”, the expansion coefficient is only shifted slightly from  $7.1 \times 10^{-6} \text{ K}^{-1}$  (“D1”) to  $7.2 \times 10^{-6} \text{ K}^{-1}$  (“D4”). The amorphous fraction of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  is depleted by the partial crystallization of the wollastonite ( $\alpha \approx 6.0 \times 10^{-6} \text{ K}^{-1}$ ). This leads to an increase of the expansion coefficient in the amorphous phase. However, stress micro or macro cracking due to different  $\alpha$ -values of the amorphous and crystalline phases was not observed in any of the samples. The expansion coefficient of sample “D4” determined by dilatometry is  $\alpha_{30-700 \text{ }^\circ\text{C}} = 7.59 \times 10^{-6} \text{ K}^{-1}$ ; this is in very good agreement with the calculated value of  $7.2 \times 10^{-6} \text{ K}^{-1}$  in view of the fact that, on the one hand, a purely amorphous phase is assumed for calculation and, on the other hand, the calculation only applies to an  $\alpha$  of 20–400 °C.

The thermal shock resistance was examined using sample “A”. It was seen under the light microscope that cracks had been produced in the sealing (Fig. 8). However, cracks were also found in the alumina so that it may be assumed that the  $\text{Al}_2\text{O}_3$  components are also susceptible to thermal shock stressing. A comparable behaviour could be expected for the other samples.

The chemical resistance after 12-h storage of the simplified sample geometry, sealed with material “A”, in 40% hydrofluoric acid showed an optical change (opaque) at the sealing but no reduction in strength or tightness.

Sample “D4” was additionally subjected to a long-time test. For this purpose, the sample material was heated from room temperature to 1300 °C in an  $\text{Al}_2\text{O}_3$  crucible, held there for 180 min and subsequently cooled to 1000 °C. This is where the long-time test for 300 h started. After this period, the sample was again cooled to RT and prepared for phase investigation. It was found that no difference between amorphous and

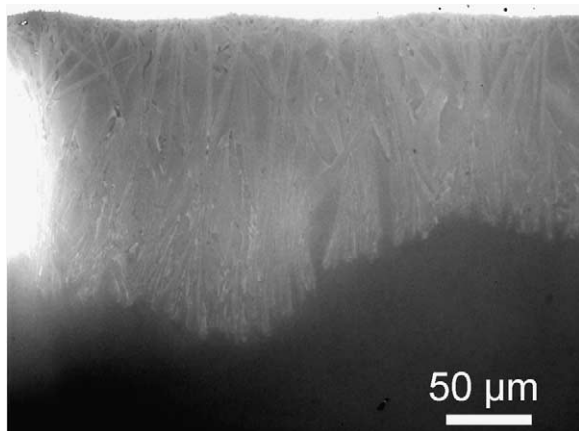


Fig. 7. Light microscopy of sample D4; dense, long crystals in the sealing material.

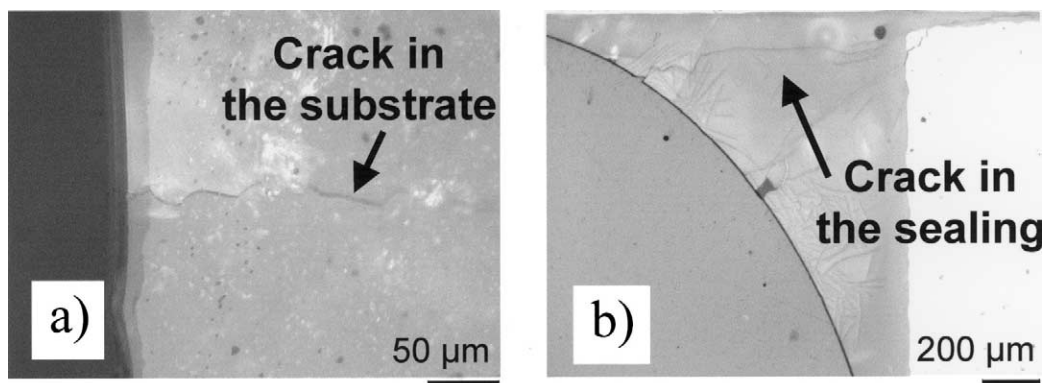


Fig. 8. Cracks in the substrate a) and the sealant b) after thermoshock test.



crystalline phase due to grinding and polishing was to be observed; only a one-minute etching with 40% hydrofluoric acid led to contrasting light microscopy images. Fig. 9b shows a light microscopy image of the sample. Dark areas (amorphous phase) as well as bright phases (crystallites) can be observed. An estimation of the area fractions is not possible with these images. No cracking or spalling due to possibly different thermal expansions occurred in this sample either.

In summary the best composition for the gastight high-temperature sealing material is composition “D4” with a maximum amount of nephelinsyenite and an optimized sintering and crystallization temperature regime.

## 5. Conclusions

A sealing compound for a ceramic compact reactor, which is gastight at operating temperatures of 1000 °C, was produced using ceramic raw materials. By varying the parameters of composition, sintering temperature and holding times it is possible to selectively crystallize wollastonite in the sealing compound. Due to intensive entanglement in the sealing gaps wollastonite increases the high-temperature resistance of the sealing. Apart from its gastightness, the sealing is chemically inert, mechanically and thermally stable. The strength values determined in 4-point bending tests at 1000 °C done in triplicate ( $\sigma_B$  between 82 and 123 MPa depending on the special composition of sample “D”) are sufficient for the planned application of the reactor. By variation of the composition it is possible to change the expansion coefficient of the sealing compound so that an adaptation to other ceramics such as mullite ceramics, porcelains or magnesium silicates is possible. The expansion coefficient of the sealing compound for the application described here is  $7.59 \times 10^{-6} \text{ K}^{-1}$  which is in quite good agreement to the sealed alumina. For that it is possible to avoid cracking due to a mismatch in the

coefficient of thermal expansion. Moreover, the material is basically suited for applications in which gastightness at elevated temperature is of significance.

The prices of the raw materials for the ceramic sealant can be seen from Table 4 (always specified by the suppliers). The tonne prices specified result in costs of <1 euro per kg of sealing compound. This amount is only a fraction of the total costs of the reactor. This means that the ceramic sealing material should be preferred to a glass sealant not only on account of its properties but also due to its economic efficiency. The selective crystallization of mullite will be investigated in additional studies.

## Acknowledgements

The authors wish to express their gratitude to the Helmholtz-Gemeinschaft Deutscher Forschungszentren (HGF, Helmholtz Society of German Research Centres) for financial support, to the Research Centre Karlsruhe (FZK) and the German Aerospace Centre (DLR) for good cooperation in the project, to the companies AKW Amberger Kaolinwerke, Quarzwerke Frechen, Süd-Chemie AG and Trukem for the raw materials and the dispersants free of charge and to Dr. R.W. Steinbrech and his group, IWV-2 Institute, Research Centre Jülich, for the high-temperature bending-strength measurements.

Table 4  
Market prices for ceramic raw materials

Raw material	Price (DM/mg)	On orders of (mg)
Kaolin Oka	363	1
Kaolin Meka	283	1
Potassium feldspar	280–400	1
Quartz	115	1
Wollastonite	2221	5

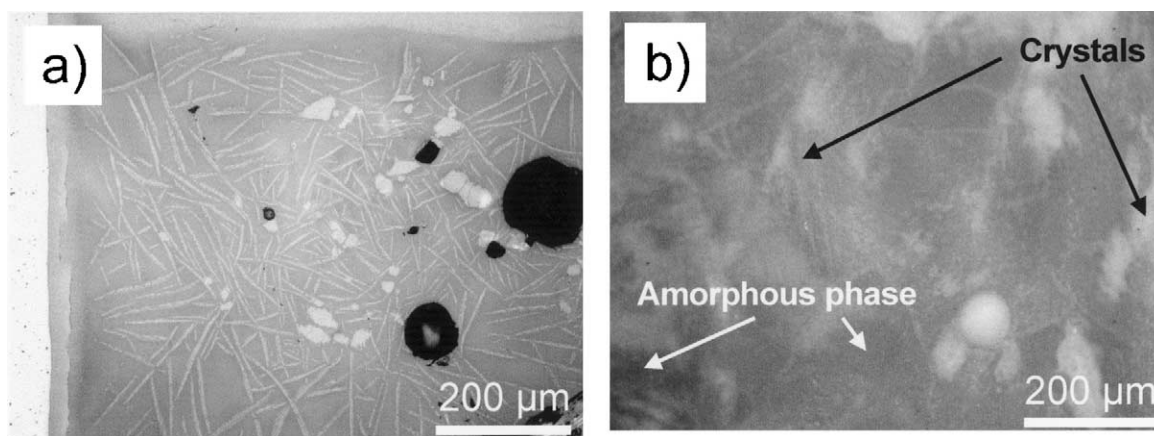


Fig. 9. Light microscopy of cyclic specimens A a) and D4 b); increasing amount of crystals belonging to the sintering variations.

## References

1. Ahn, B.-G. and Shiraishi, Y., SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> glass solder for joining of Al<sub>2</sub>O<sub>3</sub> to Al<sub>2</sub>O<sub>3</sub>. *High Temp. Mater. Proc.*, 1998, **17**(4), 209–216.
2. Locatelli, M. R., Dalgleish, B. J., Nakashima, K., Tomsia, A. P. and Glaeser, A. M., New approaches to joining ceramics for high-temperature applications. *Ceram. Int.*, 1997, **23**, 313–322.
3. Sandhage, K. H., Schmutzler, H. J., Wheeler, R. and Fraser, H. L., Mullite joining by the oxidation of malleable, alkaline-earth-metal-bearing bonding agents. *J. Am. Ceram. Soc.*, 1996, **79**(7), 1839–1850.
4. Torrecillas, R., Sainz, M. A. and Moya, J. S., Alumina-alumina and mullite-mullite joining by reaction sintering process. *Scripta Metall. Mater.*, 1994, **31**(8), 1031–1036.
5. Hauth, W. E., Ceramic-to-ceramic sealing of large shapes. *Am. Ceram. Soc. Bull.*, 1979, **58**(6), 584–586.
6. Hauth, W. E. and Stoddard, S. D., Joining of technical ceramics. International Colloquium of Ceramics. In *Glass and Metal*. Baden-Baden, Germany, 1980.
7. Hauth, W. E., Verbinden technischer Keramik/Joining of technical ceramics. *cfi/Ber DKG*, 1982, **59**(1), 12–16.
8. Knitter, R., Göhring, D., Bram, M., Mechnich, P. and Broucek, R. Ceramic microreactor for high-temperature reactions. *Proceedings of the 4th International Conference on Microreaction Technology*, 2000 Spring National Meeting, Atlanta, GA, USA, 5–9 March 2000.
9. Knitter, R., Bauer, W., Göhring, D. and Haußelt, J., Manufacturing of ceramic micro-components by a rapid prototyping process chain. *Adv. Eng. Mater.*, 2001, **3**(1–2), 49–54.
10. Schiffner, U. Verschmelzen von Gläsern für Elektrotechnik und Elektronik. HVG-Fortbildungskurs 1995. *Fügen von Glas. Hüt- tenteknische Vereinigung der Deutschen Glasindustrie*, Frankfurt, Germany, 1995 pp. 14–21.
11. Paschke, H., Fügen mit Glasphasen/joining with vitreous phases. *DVS-Berichte*, Vol. 66. Deutscher Verband für Schweißtechnik, 1985, **66**, 45–48.
12. Verband der Keramischen Industrie e.V. (VKI). Brevier Technische Keramik. 2. Überarbeitete Auflage, VKI Informationszentrum Technische Keramik, Schillerstrasse 17, 95100 Selb, Germany, 1998, p. 78.
13. Carty, W. M. and Senapati, U., Porcelain—raw materials, processing, phase evolution, and mechanical behavior. *J. Am. Ceram. Soc.*, 1998, **81**(1), 3–20.
14. Castelein, O., Soulestin, B., Bonnet, J. P. and Blanchart, P., The influence of heating rate on the thermal behaviour and mullite formation from a kaolin raw material. *Ceram. Int.*, 2001, **27**, 517–522.
15. Appen, A. A., *Chemie des Glases*, 2nd edn. Russian Federation, Verlag Chemie, St. Petersburg (Leningrad), 1974.
16. Zwetsch, A., Dilatometrische Messungen an keramischen Rohstoffen. *Ber. DKG Bd*, 1955, **32**(3), 63–69.