High Temperature Ceramics for Light-Weight Kiln Furniture

Alumina- and mullite-based materials for kiln furniture application of up to 1700 °C have been successfully developed. The materials show significantly improved thermomechanical properties in comparison to commercial benchmark products permitting the design of kiln furniture with reduced mass. This leads to significant energy savings in high temperature processes. It is demonstrated that the achieved improvement in corrosion resistance against lead-containing vapours increase the lifetime of the products considerably.

Fig. 1
Examples for RAMUL components

Fig. 2
RAKOR saggars and firing props

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Introduction

About one third of the energy consumed within the manufacturing industry is used in high temperature processes with temperatures above 1000 °C [1, 2, 3]. Especially in the ceramic, glass and cement industries, large amounts of energy are consumed. Energy efficiency is one of the key parameters to reduce energy consumption and therefore CO_2 emissions [3, 4]. There are several measures to realize energy savings [5]. One possibility is to reduce the thermal mass of kiln furniture in thermal processes [5, 6]. Kiln furniture is used to carry the products in the furnace during the thermal treatment. During sintering processes, the mass of the kiln furniture can be up to 80 % of the

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energy saving, saggars, firing props, kiln components, thermomechanical properties, creep resistance

Fig. 3
Thermo-optical measuring (TOM) device TOM_air used for measuring the uniaxial viscosity of the materials

total mass of the kiln charge. This leads to long process cycles, large energy consumption and an irregular energy input into the products. To reduce the mass of the kiln furniture, two strategies are followed: a design approach and a material approach. The first approach is to optimise the design of the kiln furniture, e.g. thinner walls, combination of different materials, etc. [7]. The design approach is often limited by the high temperature performance of the materials used for the kiln furniture [8]. Thus, the second approach is to improve the materials for the kiln furniture, especially their high temperature properties [9].

The objective of the collaboration between Paul Rauschert Steinbach GmbH and Fraunhofer Center for High Temperature Materials and Design HTL was to develop alumina and mullite-based kiln furniture materials with improved high temperature performance. The aim was to develop kiln furniture with outstanding thermomechanical properties to be used at application temperatures above 1600 °C. A material index was derived to evaluate the performance of the developed materials and to compare it to commercial benchmarks. The improvement in the high temperature properties enables a mass reduction of the kiln furniture on the total kiln charge and therefore saves energy. The new materials RAMUL, RAMUL-HT and RAKOR were successfully engineered to satisfy these requirements (Figs. 1–2).

Evaluation of performance of kiln furniture materials by material indices

To be able to evaluate and compare the performance of different kiln furniture materials, a material index was developed [10]. For this purpose, kiln furniture in form of a plate carrying a load at high temperatures was considered. Ideally the deformation and the mass of the plate should be as low as possible. In practice, a reduction of the mass can be realized by decreasing the density, e.g. by increasing the porosity, of the material and/or reducing the thickness of the plate. In both cases, the deformation of the plate will typically increase. To find an optimum trade-off between these different requirements, the following material index I can be used [10]:

$$I = (c_\rho * \rho)/\eta^{1/3}$$

Here, c_ρ, ρ and η are the specific heat capacity, the density and the uniaxial viscosity, respectively. An improvement in the performance of the material like increased creep resistance and reduced density leads to a lower value of the material index I. Even though the density and hence the mass of the new materials RAMUL, RAMUL-HT and RAKOR was reduced, the creep resistance could still be improved. The density ρ of the material was measured by the Archimedes principle. The values of the heat capacity c_ρ of the corresponding phases were taken from Barin [11]. The uniaxial viscosity of the materials for the different temperatures was determined using a thermo-optical measuring (TOM) device developed at Fraunhofer Center HTL [12] (Fig. 3).

For these measurements, the samples were cut to rectangular or cylindrical specimens dependent on the manufactured shapes. Rectangular blocks had dimensions of 8–10 mm both in length and width and a height of 15 mm. They were cut from samples with plate geometry. Cylindrical specimens had a diameter of 8 to 10 mm and a height of 15 mm and were cut from rod-shaped samples.

The cut specimens were placed between a lower and an upper piston into the TOM device. Loads of 50 to 200 N corresponding to compressive stresses of 1 to 3 MPa were applied to the specimens. The samples were fired at 1250 °C with a dwell time of 1 h. After that, the temperature was slowly increased in 50 °C steps to a maximum temperature of 1500 °C. At all 50 °C steps, the samples were dwelled for 1 h and the sample height was continuously monitored. From the change of the sample height with respect to time, the creep rate ε' was derived. The uniaxial viscosity at a given temperature was calculated by dividing the stress σ applied to the sample by the creep rate.

$$\eta = \frac{\sigma}{\varepsilon'}$$

Comparison of product performance with commercial benchmarks

To evaluate the material performance of the developed materials RAMUL, RAMUL-HT and RAKOR, the material index I was determined for these products and compared to similar benchmark materials available on the market. Furthermore, the bulk density, porosity and bending strength were measured for material characterization and comparison. Fig. 4 shows the material index I for the mullite-based kiln furniture materials RAMUL and RAMUL-HT in comparison to a simi-

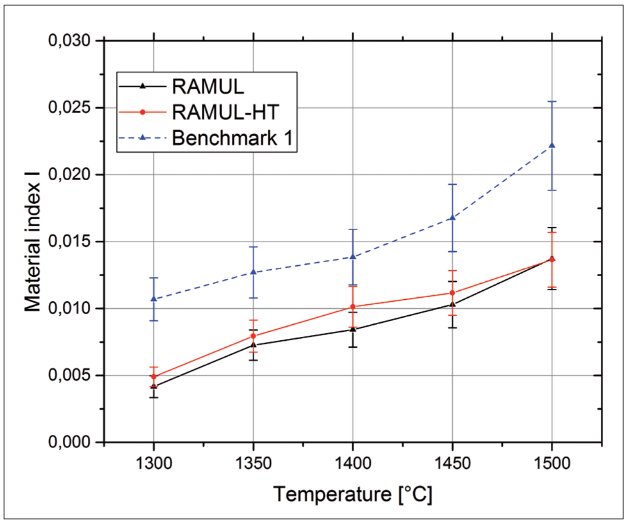

Fig. 4
Comparison of material index I of RAMUL and RAMUL-HT with selected benchmark product determined in a temperature range 1300–1500 °C

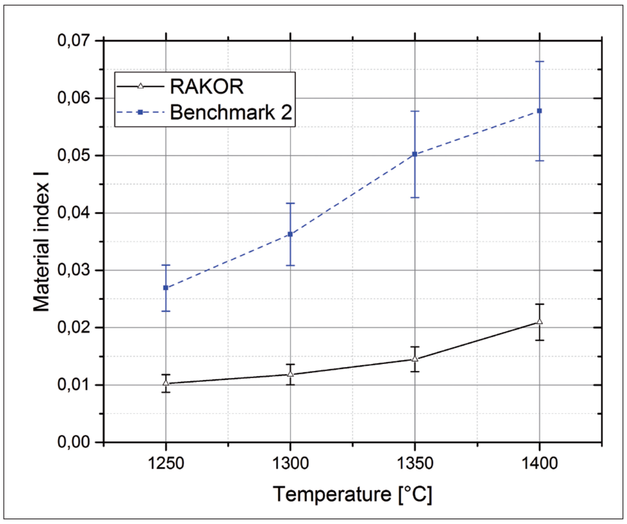

Fig. 5
Comparison of material index I of RAKOR with selected benchmark product determined in a temperature range 1250–1400 °C

lar commercial benchmark product. Both RAMUL and RAMUL-HT exhibit a significantly lower value for the material index I than the commercial benchmark product. At 1500 °C, a reduction of the material index I of almost 40 % could be achieved. Fig. 5 shows the material index I for the alumina kiln furniture material RAKOR in comparison to an equivalent commercial benchmark product. For the relevant temperature range of 1250–1400 °C, a reduction of the material index I of 60 % was achieved. These results demonstrate the improved performance of the developed materials for the application as kiln furniture at high temperatures. Tab. 1 summarizes some properties of the materials RAMUL, RAMUL-HT and RAKOR.

Creep resistance and mechanical durability at high temperatures up to 1700 °C

RAMUL and RAMUL-HT have an excellent creep resistance which is demonstrated in a low material index value. For rod-shaped samples, even at very small sample diameters, the creep deformation is quite low in comparison to alternative benchmark products. To evaluate those characteristics experimentally, rods made from RAMUL had been extruded with a diameter of 3,3 mm to test the creep deformation according to DIN EN 820-4 and compare the results to benchmark products with the same dimensions.

The end of the rods were placed on two supports in a laboratory furnace and a typical kiln cycle of 24 h cold-cold with a maximum temperature of 1600 °C was applied. After five cycles the RAMUL rod did not show any sign of deformation whereas the benchmark rod showed significant deformation (Fig. 6).

Tab. 1
Properties of RAMUL, RAMUL-HT and RAKOR

Properties	**RAMUL**	**RAMUL-HT**	**RAKOR**
Bulk density [g/cm³]	2,1	2,2	2,3
Porosity [%]	30	37	40
Max. operating temperature [°C]	1600	1700	1700
Al_2O_3 content [%]	79,7	88,4	99,43
SiO_2 content [%]	19,8	11,16	0,29
Bending strength 20 °C (3-point) [N/mm²]	31	25	44
Material index I at 1500 °C measured by Fraunhofer-Zentrum HTL at 1400 °C	0,0138 –	0,0136 –	– 0,021

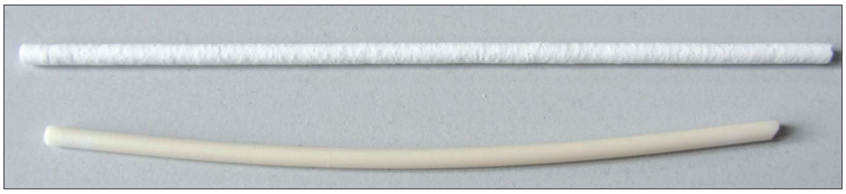

Fig. 6
Solid rods (diameter 3,3 mm) made out of RAMUL-HT (top) and a benchmark material (bottom) after five kiln cycles at a dwell temperature of 1600 °C

Depending on the application and shape of the RAMUL and RAKOR products, a total weight reduction between 20–50 % could be achieved at consistent or even improved thermomechanical properties. Taking into consideration the lower mass of the kiln furniture in relation to the sintering goods, less energy is consumed when applying the newly designed materials as firing auxiliaries.

RAMUL can be operated at temperatures up to 1600 °C. RAMUL-HT and RAKOR can be applied up to a temperature of 1700 °C. Hence, those newly engineered products show a significantly improved performance in comparison to the benchmark products, saving energy and reducing costs.

Excellent chemical resistance of RAKOR in lead containing atmospheres during production of piezo- and PTC-ceramics

Applying an all corundum raw material, RAKOR has good corrosion resistance against numerous substances. During sintering of piezo- and PTC-ceramics, the kiln atmosphere commonly contains lead oxide (PbO) vapour which forms from the various raw materials applied. The evolving PbO vapours are reacting with the saggar material forming lead silicate and lead aluminosilicate phases. These reactions have a negative impact on creep deformation as well as crack formation and usually induce early failure. At the end of their life span, ordinary saggars contain about 25 % lead and have to be disposed as hazardous waste. To demonstrate the advantages of RAKOR, long-term test series have been carried out in two atmospheres containing different amounts of lead. One saggar was used in a tunnel furnace with a concentration of 6–12 mol-% $PbTiO_3$ and the other one was used in a laboratory furnace with a higher concentration of 15–20 mol-% $PbTiO_3$, both at temperatures around 1300 °C.

After these tests, investigations with x-ray diffraction showed that the RAKOR refractory material did not contain significant amounts of lead-containing phases. These results indicate the improved corrosion resistance of RAKOR in comparison to the benchmark materials. Ceramic-based saggars used for sintering lead containing ceramics usually have to be replaced after an average of 30 kiln cycles as a result of severe cracking and mechanical failure due to the strong corrosion from PbO vapours. However, both RAKOR saggars performed 72 kiln cycles until failure compared to 30 cycles for the standard benchmark saggar. Due to its high purity, RAKOR only absorbs very low amounts of lead, hence toxic waste can be reduced drastically and lifetime extended by a factor of roughly 2,5.

Application and product examples

RAMUL and RAKOR particularly qualify as firing auxiliaries at high temperatures with very good creep resistance. Typical application examples for these materials are saggars, exhaust air pipes, firing props, kiln components, crucibles and many more (Fig. 1–2). Through the use of various shaping techniques, a variety of different geometrical forms can be realized. General production methods are extrusion, dry and wet pressing as well as slip casting. Based on the very low shrinkage of these materials, a near-net-shape production is possible.

RAKOR is especially suitable for aggressive atmospheres like lead containing vapours evolving during the sintering process of PTC- and piezo-ceramics due to its chemical and corrosion resistance. Hence, saggars and firing props are an ideal application for this kind of new material. Fig. 2 shows several RAKOR products, e.g. different types of saggars, round and square shaped props with and without holes.

Fig. 1 shows various examples of RAMUL and RAMUL-HT products like thin- and thick-walled pipes, square, round and multihole tubes and also collar pipes,

Fig. 7
Kiln components like exhaust collar pipes and firing props

Fig. 8
RAKOR multi-platform racks for sintering smaller parts

which can be obtained after grinding extruded profiles. Many other geometries can be manufactured with diameters from a few millimetres and up to 150 mm.

RAMUL-HT was specifically designed for long-time stability and thermal shock resistance for temperatures up to 1700 °C. One typical application would be for kiln components like exhaust pipes, which are under highest thermal stresses, since they are placed between the hot interior of the kiln and the cold ambient air (Fig. 7). When combining ceramic plates and beams, advanced kiln furniture like complex rack structures as shown in Fig. 8 could be implemented. These multi-platform racks are especially useful for sintering smaller parts, e.g. made by CIM or MIM (ceramic or metal injection moulding). Having several thin-walled stacks close together means reducing the mass of the kiln furniture and sintering more parts at once. Thus, energy can be saved and consequently CO_2-emissions are reduced.

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