A Novel Processing Route for Alumina/Mullite-Based Refractory Materials

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The paper describes a novel processing method for the manufacturing of alumina/mullite composite materials. It makes use of a dissolution process of aluminium isopropylate and a subsequent, but slow increase of the pH value in the processing solution by stepwise addition and decomposition of urotropine. The pH value increase results in a precipitation of aluminium hydroxide, and in the presence of mullite particles and alumina particles a homogeneous solid body is formed after hydrolysis and drying. While it is not possible to obtain intact samples without alumina addition the combined presence of alumina and mullite particles lead to intact and crack-free parts even after sintering at 1650 °C.

1 Introduction

There is an increasing need in carbon-free refractory materials, e.g. for steel casting. One of the promising candidates for this purpose is mullite, which is a binary oxide ceramic material with a composition varying from $3Al_2O_3 \cdot 2SiO_2$ to $2Al_2O_3 \cdot SiO_2$. Technical mullite possesses a variety of mechanical properties desired for high temperature applications such as a good thermal shock behaviour, low thermal conductivity, good creep resistance, high chemical and thermal stability, good mechanical strength in harsh environments, and low thermal expansion. This makes mullite ceramics interesting candidates for different applications under thermal and mechanical load, e.g. for engine components, catalyst supports, thermal insulation parts, gas filter supports or heat exchangers [1–5].

However, plain mullite ceramic materials possess low fracture toughness, and material failure often occurs when heating or cooling rates are too high. An alternative is a material with a reinforcement phase [6]. One of these reinforcement phases is alumina. This is due to its high flexural strength, fracture toughness, melting temperature, hardness as well as its good cor-

rosion behaviour and wear resistance in comparison to mullite. A few reports on alumina-mullite composites have demonstrated better mechanical properties compared to non-reinforced mullite [7–10].

In this work a novel processing method for the manufacturing of mullite/alumina parts is presented. It makes use of a dissolution/precipitation process for the generation of an alumina matrix which embeds the mullite particles.

2 Experimental

Aim of this work was to manufacture a mullite/alumina composite material with mullite embedded as particles in an alumina matrix; the alumina matrix is generated by a dissolution/precipitation process, while the mullite particles (or mullite and alumina particles) are introduced into the sol-gel matrix by dispersion. Two different process strategies were carried out. In a first series only mullite particles were used and in a second approach mullite particles and alumina particles were used simultaneously as the particulate phase.

2.1 Sample preparation

As alumina source aluminium triisopropylate, $(Al(i-C_3H_7-O))_3$, 98 %, referred to as

Al-iPr, was used. Al-iPr was dissolved in isopropanol (99 %) under vigorous stirring with a magnetic stirrer at 50 °C in a closed vessel for several hours. The Al-iPr concentration was adjusted to 0,5, 1,0 and 1,5 mol/l respectively, which corresponds to 25,5 g, 51,0 g and 76,5 g alumina per liter aluminium triisopropylate solution, respectively.

After the dissolution process mullite particles (SYMULOX M72 K0, Nabaltec AG/DE) or a mixture of mullite and alumina particles (NABALOX NO 783) were added and the hydrolysis and gel formation process of the dissolved Al-iPr was started by the addition of an aqueous urotropine (hexamethylene tetramine, $N_4(CH_2)_6$, 99 %) solution. When alumina and mullite were added at the same time, the weight ratio of both was 50 %, and the total amount of fillers (related to the weight of the filled system) was varied between 25 – 55 mass-%.

Urotropine, Al-iPr and isopropanol were obtained from Merck Schuchardt OHG/

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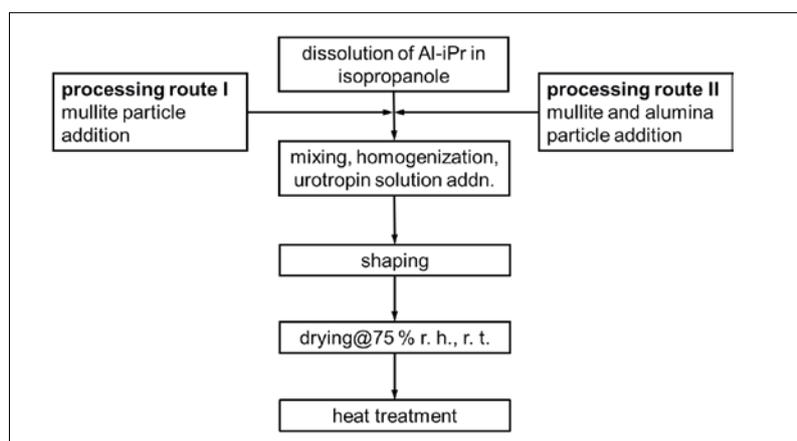E-mail: m.scheffler@ovgu.de

Fig. 1 Processing scheme of the sample preparation (r. h. – relative humidity; r. t. – room temperature)

DE. The concentration of the urotropine solution was 7 g/l. When the urotropine solution was mixed with the Al-iPr solution, the molar ratio of water to Al-iPr was varied between 2,8 – 5,0.

This actually resulted in a nominal alumina amount derived from the sol-gel process (hydrolysis of Al-iPr, condensation of alumina-hydroxy species and formation of α-alumina after drying/during sintering) between 18 – 26 mass-% alumina or 4,6 and 6,6 vol.-%, respectively, corresponding to the system without any other particles.

SYMULOX M72 is a sintered mullite consisting of 72 mass-% alumina, 26 mass-% silica, 0,6 mass-% K_2O, 0,3 % Fe_2O_3, the balance is Na_2O, TiO_2, CaO and MgO. It has a crystallinity of 90 – 95 % and the amount of glass phase is 5 – 10 %.

The particle size analysis showed a $d_{50} = 3 – 5$ μm [11]. XRD investigations have shown an amount of 4 mass-% of α-alumina within this starting material. The NABALOX NO 783 alumina possesses a purity of 99 %, and a monomodal particle size distribution with $d_{50} = 0,83$ μm [12].

From XRD and Rietveld analysis a composition of 86 mass-% corundum and 14 mass-% transition alumina (θ-Al_2O_3) was determined.

During the urotropine addition the pH value changed from 2,8 (dissolved Al-iPr in isopropanol) to about 5 – 6 after urotropine addition.

During the increase of pH value an increase of the vsicosity was observed leading to a point where the magnetic stirrer did not work anymore. In order to continue the mixing, hydrolysis and gelation process the slurry was transferred to a planetary centrifugal mixer (Thinky Mixer ARE 250, Thinky Corporation/JP), and processed for 5 min at a rotational speed of 1500 rpm. After processing in the thinky mixer the slurry was poured into a cylindrical teflon mold with 10 mm or 20 mm in diameter and 40 mm in length, and transferred into a dessicator for ongoing gel formation and sample drying. The desiccator was operated under controlled humidity.

The samples were dried first for one week at a relative humidity (r. h.) of 75 % (the r. h. was adjusted with a saturated sodium chloride solution) and another week at 43 % r. h. (a saturated potash solution, K_2CO_3).

After withdrawal from the desiccator the samples were dried at 110 °C for 24 h in a drying furnace and subsequently sintered in air. The heating rate for the sintering process was 5 K/min up to a peak temperature of 1600 °C and a hold time of 3 h or 6 h. A processing scheme is given in Fig. 1.

2.2 Sample characterization

The samples were characterized with respect to their shape retention, shrinkage and phase composition. For the determination of the volume shrinkage the geometrical data after shaping, drying under controlled humidity and after sintering were recorded.

Crystalline phases were analyzed with a X-ray diffractometer with Cu-Kα_1/α_2 radiation (X'Pert, PANalytical GmbH/DE) and the phase amount was quantified with Rietveld analysis using the Topas Academic 5 package (Coelho Software/AU).

Selected samples were investigated with scanning electron microscopy (REM, XL 30 ESEM, FEI/US) equipped with an EDS analysis system (EDAX/DE).

3 Results and discussion

The hydrolysis of the Al-iPr and the subsequent precipitation can roughly be described as a three-step mechanism. The first step is the hydrolysis of the Al-iPr as described in eq. 1:

$$Al(i\text{-}C_3H_7\text{-}O)_3 + H_2O \rightarrow$$
$$[Al(H_2O)_6]^{3+} + 3\ OH^- + 3\ C_3H_7OH \qquad (1)$$
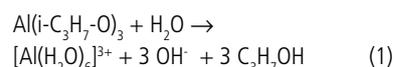
This reaction occurs when the urotropine solution is introduced into the Al-iPr/particle-loaded mixture. In a second step urotropine hydrolyses partially into ammonia (NH_3) and formaldehyde, see eq. 2:

$$N_4(CH_2)_6 + 6\ H_2O \rightarrow 4\ NH_3 + 6\ HCHO \quad (2)$$
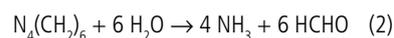
While the pH value in the aluminium hydroxide solution is slightly acidic (~3), the addition of urotropine leads to a slow and homogeneous increase of the pH value over the entire volume of the solution to about 4 – 5, which covers the theoretical range of precipitation of aluminium hydroxide over a wide concentration range. This leads slowly to the formation of the non-soluble aluminium hydroxide, actually resulting in a fluffy precipitate, see eq. 3:

$$[Al(H_2O)_6]^{3+} \rightarrow [Al(OH)_3(H_2O)_3]\downarrow + 3\ H^+ \quad (3)$$
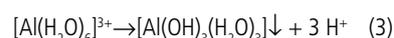
The main advantage of the use of urotropine for the precipitation of the aluminium hydroxy gel in comparison to ammonia results in a comparatively low pH value; the precipitate will not redissolve to form the tetrahydroxyaluminate complex $[Al(OH)_4]^-$ and homogeneously distributed seeds may lead to a narrow particle size distribution of the precipitate [13].

While in the sample series without alumina fillers it was not possible at each processing step to obtain crack-free samples, the investigations were focused on the sample series with mullite and alumina particles. Fig. 2 shows a typical example of a disk after hydrolysis/precipitation and drying right after removal from the desiccator (l.) and after additional drying in air (r.). In the as-removed samples some cracks are visible
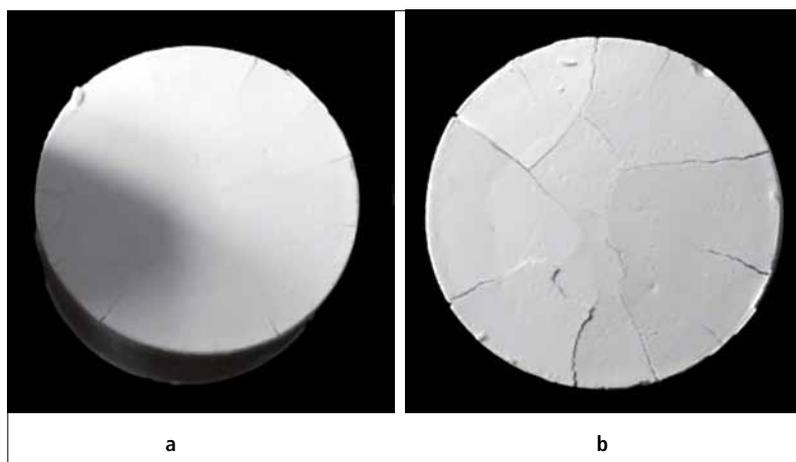
Fig. 2a–b Alumina particle-free samples after withdrawal from the desiccator (a), and after drying in air (b)

Fig. 3 Photograph of a mold (l.), a sample after withdrawal from the desiccator (middle), and a sample after sintering at 1650 °C for 3 h (r.); all samples prepared with both alumina and mullite particles
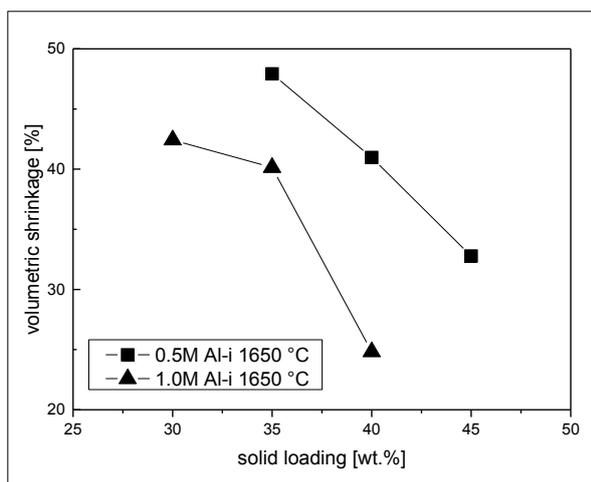

Fig. 4 Volume shrinkage as a function of the solid load; the n_{H2O}/n_{Al-iPr} ratio was 2,8; all samples sintered at 1650 °C for 3 h
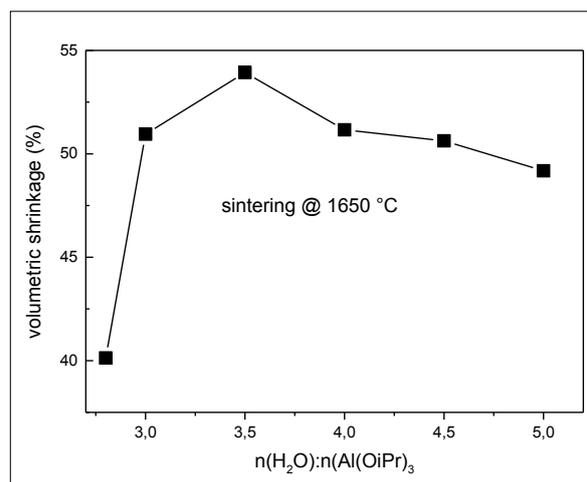

Fig. 5 Volume shrinkage as a function of the n_{H2O}/n_{Al-iPr} ratio; all samples were prepared with 35 % solid load of a 1 mol/l Al-iPr solution; sintering was carried out at 1650 °C for 3 h

starting at the outer rim. After drying these cracks have propagated throughout the entire sample; thus, sintering was carried out only for the purposes of phase analysis.

Fig. 3 shows a sample filled with mullite and alumina particles. Most of the samples with both, mullite and alumina fillers, were intact after withdrawal from the desiccator and also after sintering. No cracks were visible. However, the shrinkage was high, ranging between 25 – 55 vol.-%.

Three series of samples were prepared and investigated with respect to their shrinkage behaviour. In two series the total solid load of the 50 : 50 mixture (by weight) of mullite and alumina particles was varied from 35 – 45 % for the Al-iPr solution with a concen-

tration of 0,5 mol/L and from 30 – 40 % for the Al-iPr solution with a concentration of 1,0 mol/l. In both series a decrease of the volume shrinkage was observed with an increase of the total filler concentration. In the system with a higher Al-iPr concentration (here: 1,0 mol/l) the volume shrinkage is lower compared to that of the series with the lower Al-iPr concentration (Fig. 4). This indicates a higher total amount of solids in the system after removal of the liquid phase (isopropanol) actually originating from higher load of Al-iPr.

In a third sample series the shrinkage was investigated as a function of the water-to-Al-iPr ratio. An increase of the volume shrinkage was observed from $n_{H2O}/n_{Al-i} =$

2,8 – 3,5 resulting in a volume shrinkage of 40 and 57 %, respectively. Higher n_{H2O}/n_{Al-i} ratios lead to a slight decrease of the shrinkage (Fig. 5). The porosity, however, was not measured.

The shrinkage behaviour of these three sample series indicate a set of complex dependencies of the processing parameters on the resulting microstructure, e. g. the hydrolysis kinetics of the Al-iPr as a function of the temperature, the decomposition kinetics of urotropine and the resulting ammonia and formaldehyde formation, the resulting pH value in the solution/dispersion system and the parameters of the drying process.

X-ray powder diffraction analyses have identified alumina and mullite as the only
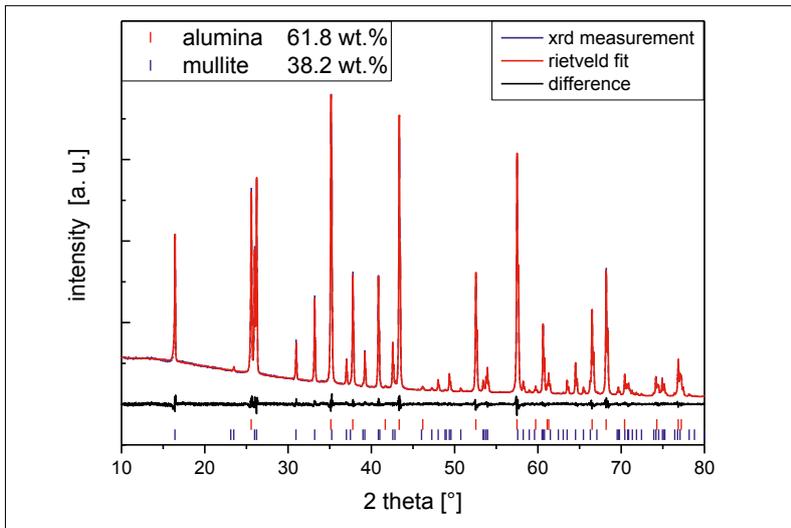
Fig. 6 XRD powder patterns of a sample prepared with a 1,0 mol/l Al-iPr solution, a n_{H2O}/n_{Al-iPr} ratio of 2,8 and a 40 % solid load after sintering at 1650 °C for 3 h. The volume fraction of alumina and mullite corresponds to 56,2 % and 43,8 %, respectively

crystalline phase for all samples, and by means of Rietveld analyses the amount of both components was calculated. A typical X-ray diffraction pattern, the related Rietveld fit and the differences between experimental and fitted data are shown in Fig. 6. However, the amount of the glassy phase as described in the data sheet for the SYMULOX 72 mullite material [11] was not analyzed. It also has to be noted, that the deviations from the calculated and the measured phase amounts were small. For instance, a sample prepared from mullite particles and a Al-iPr solution sintered at 1600 °C for 3 h with a calculated amount of alumina and mullite of 51,4 mass-% and 48,6 mass-% actually showed 52,0 mass-% alumina and 48,0 mass-% mullite after the Rietveld fit.

This is, in contrast to systems were silicon alcoholates are used for sol-gel processing, e. g. in [14], of advantage: aluminium triisopropylate does not show loss during processing due to its high melting or boiling point. It remains completely in the system prior to and after the hydrolysis. Tetraethyl orthosilicate, in contrast, may evaporate at elevated temperatures thus resulting in uncertaincies in a subsequent analysis of the composition.

Fig. 7 shows SEM images of selected samples. The samples possess a high amount of porosity (l.). In Fig. 7 (r.) a mullite particle is surrounded by alumina, as detected by EDS analysis.

4 Conclusion

A novel processing method for the manufacturing of alumina/mullite composite materials has been demonstrated. It makes use of dissolved aluminium triisopropylate as alumina source, particulate mullite and alumina fillers and a complex set of chemical reactions during the addition of an aqueous urotropine solution. The mechanism of the liquid-to-solid transformation is roughly divided into three steps: in step (1) the Al-iPr hydrolyses to form solvated aluminium cations, in step (2) the urotropine decomposes to form formaldehyde and ammonia actually resulting in an increase in the pH value and in a 3rd step (3) the non-soluble aluminium hydroxide is formed leading to an increase in the viscosity of the system. The aluminium hydroxide covers the mullite and/or alumina particles and a drying process lead to the reduction of moisture in the system.

The loss of three isopropanol molecules during hydrolysis of the Al-iPr results in an immense weight loss, which, in turn, leads to a high volume shrinkage of up to 55 % and a remaining porosity even after sintering at 1650 °C.

While mullite-filled materials show cracks already after drying, samples filled with mullite and alumina were intact even after
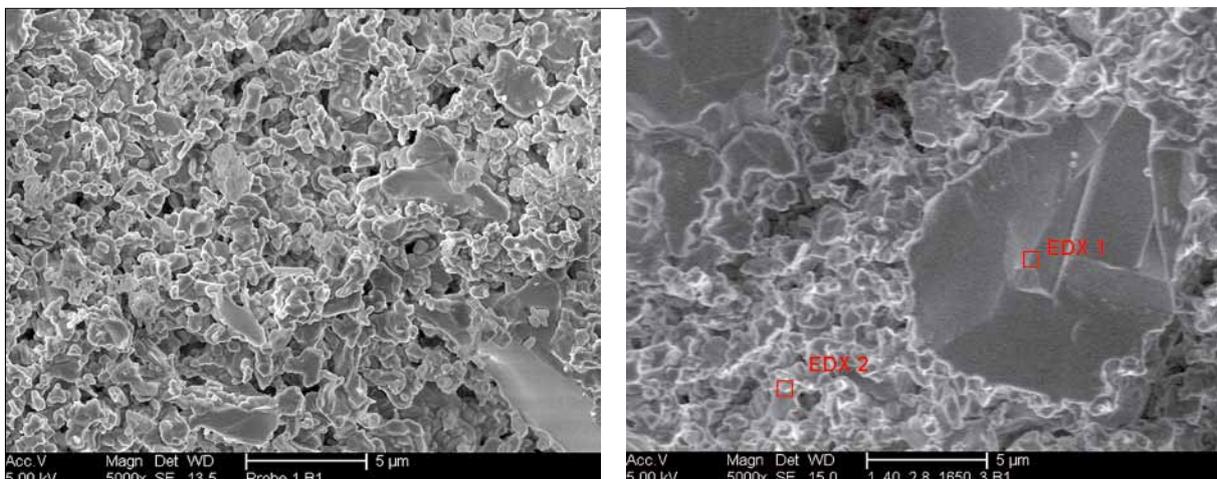

Fig. 7 Typical microstructure of sintered samples: SEM image of a sample prepared with a 0,5 mol/l Al-iPr solution, a n_{H2O}/n_{Al-iPr} ratio of 2,8 and a 55 % solid load (alumina and mullite) after sintering at 1650 °C for 3 h (l.); SEM image of a sample prepared with a 1,0 mol/l Al-iPr solution, a n_{H2O}/n_{Al-iPr} ratio of 2,8 and a 40 % solid load after sintering at 1650 °C for 6 h (r., the spots inside the right image indicate mullite – EDX 1 – and alumina – EDX 2 –)

sintering. This effect is not clear yet and needs more attention in ongoing work.

The only crystalline phases found in XRD are alumina and mullite. Due to the nature of the Al-iPr, no loss of alumina was observed during processing, and the amount of both phases as measured by Rietveld analysis is in good agreement with the calculated phase amount for the synthesis of the material.

This work shows the feasibility of refractory processing with aluminium alcoholates under controlled dissolution and pH variation. There are, however, a set of parameters such as the hydrolysis kinetics of the Al-iPr, the decomposition kinetics of the urotropine, the role of water and isopropanol during processing and their influence on the material microstructure and properties, which have not yet been addressed.

Acknowledgement

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