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Aqueous tape casting of reaction bonded aluminium oxide (RBAO)

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Abstract

Reaction bonding of alumina (RBAO) has been proved to be a successful route to make high-performance alumina. However, the aluminium metal in the starting mixtures prevents using aqueous processing techniques in the initial phase. Here a route is presented for aqueous tape casting of RBAO by hydrophobization of the starting powder and preparing a suitable tape cast suspension. Thermal analysis (TGA/DSC) showed that it is possible to combust the organic phase prior to oxidation of the aluminium, opening routes to laminated ceramic-metallic composites. TGA/DSC combined with imaging (SEM) and phase analysis (XRD) also showed that the oxidation of the aluminium in RBAO occurs in two steps. Sintering experiments showed anisotropic grain growth at 1550 °C, resulting in a lower density than sintering at 1500 °C or 1600 °C. The bending strength of the sintered tape increased with temperature, resulting in a bending strength of 290 MPa after sintering at 1600 °C.

Keywords: Tape casting; Suspensions; Sintering; Al_2O_3; RBAO

1. Introduction

Tapecasting is widely used within the industry for making large thin sheets of ceramic materials for the fabrication of ceramic substrates, multilayer products, piezoactuators, sensors, etc.[1–4] Typically, during tape casting, a slurry consisting of the ceramic powder dispersed in a solvent, with the addition of dispersants, binder and plasticizer, is cast onto a moving or stationary substrate. The cast is then dried, if necessary laminated, and finally sintered to obtain a flat ceramic sheet. The thickness normally varies from 100 to 300 μm, but thinner tapes down to 5 μm and thicker tapes up to several mm have been obtained.

Traditionally, tapecasting involves organic liquids as dispersing medium, but currently the trend is to move away from organic solvents towards water based systems. The main reason for using water based systems is the low toxicity, low cost and the reduction of environmental risks.[4] The disadvantages of using water based systems, however, are the slower drying rate and the higher chance of cracking during drying compared to the commonly used organic solvent based systems.

The reaction bonding of aluminium oxide (RBAO) has been proposed by Claussen as an attractive method for producing alumina.[5] Compared to conventionally processed alumina, this reaction bonded material exhibits several advantages, such as a lower processing temperature, near net shape forming capability and superior mechanical properties. In short, the RBAO process begins with a compact made from a mixture of aluminium and alumina powder. During heating in air, the Al particles are first oxidized in the solid state up to a temperature of 660 °C, the melting point of aluminium, forming a particle with an aluminium core and a alumina shell. Above 660 °C the aluminium becomes liquid and a second oxidation step is possible. The final composite is a monolithic Al_2O_3 component.

However, combining tapecasting with RBAO presents the problem of limited chemical stability of fine, milled aluminium particles in water against hydrolysis. Therefore a surface treatment of the milled powders is necessary. Since this problem is also present in the aqueous processing of aluminium nitride and aqueous gel casting of RBAO,[6] the solution can be expected to be the same. For these systems[7–9] it has been shown that carboxylic acids considerably improve the chemical stability against hydrolysis, in particular stearic acid. Unfortunately, the drawback of this process is that the powder becomes hydrophobic and consequently largely nondispersible in water unless the proper dispersant is used.

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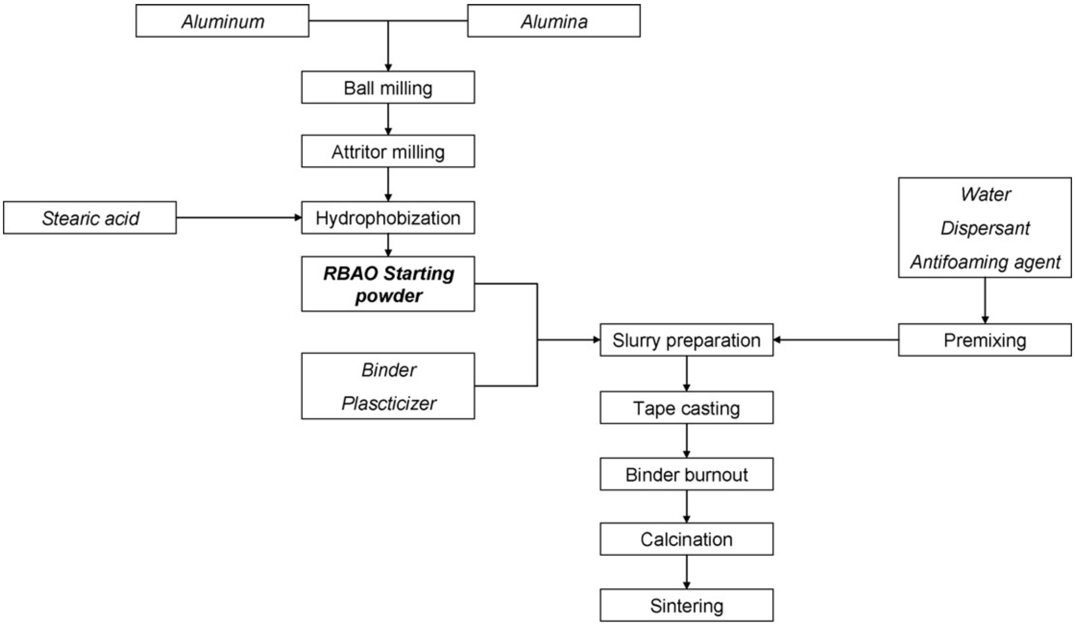

Fig. 1. Schematic representation of the process.

In this paper a successful route for tapecasting RBAO powders is presented and some properties of the resulting ceramic evaluated.

2. Experimental

The experimental procedure is depicted in Fig. 1.

A mixture of 100 g consisting of aluminium (VLT515, Pechiney, 10 μm) and alumina (Amperit 740.0, H.C. Stark, 22.5 μm) is ball milled in polyamide jars with acetone as milling medium and yttrium stabilized zirconia balls for 8 h. After drying the mixture in air, it is subsequently attritor milled for 6 h to reduce the particle size to <1 μm. The alternative of using 1 μm Al powder is rather expensive, rendering an ineconomical process.

The next step in the process is the hydrophobization of the powder with stearic acid. To this purpose 7 g of stearic acid is dissolved in 100 g warm acetone (∼40 °C) and added to 125 g of powder mixture and subsequently freeze dried, resulting in the RBAO starting powder. In the next step the slurry was prepared by premixing water, dispersant (EMPHOS CS-1361, ART) and antifoaming agent (DB-310, Dow Corning), followed by the simultaneous addition of the RBAO starting powder, binder (Mowilith DM765, Celanese) and plasticizer (polyethylene glycol (PEG) 400, Merck). The normal procedure in which the starting powder is added in the first step was not possible, due to the low amount of water used in the first step to prevent cracking of the green tape. The mixture was subsequently ball milled for 10 min to create a homogeneous slurry, avoiding to destroy the stearic acid coating by stirring too vigorously or too long. In the final preparation step, the slurry was slowly rolled for at least 24 h for deairing.

Tapecasting (TCW TTC-1200) was done with a gap height of 0.50 mm, width 10 cm and a carrier film speed of 28 cm/min using a single doctor blade. After drying in air, the binder burnout was combined with the calcination of the compact and was done at 1 °C/min up to 1200 °C in air. Sintering was done in air at 1500 °C, 1550 °C and 1600 °C for 4 h.

Characterization of the slurry and slurry components has been done by rheology (Haake Rheostress RS 100) and zeta potential measurements with ESA (Electrokinetic Sonic Amplitude, Colloidal Dynamics ZetaProbe). Thermal analysis was done with combined differential scanning calorimetry / thermogravic analysis (DSC/TGA, Netsch STA 449C Jupiter) and XRD (Rigaku Geigerflex). Imaging was done with scanning electron microscopy (SEM), both in lower secondary electron image mode (LEI, Jeol JSM-6340F) and backscattered electron image mode (BEI, Jeol JSM-840A). Four point bend strength was done (Instron 1195) using samples for each sintering temperature.

3. Results and discussion

3.1. Zeta potential of RBAO

In order to make high performance ceramic suspensions, it is important to choose the right pH. In a suspension two forces play an important role, the attractive Van der Waals forces between the particles and the electrostatic repulsion or attraction of charged particles characterized by the zeta potential[10]. The latter force is largely influenced by the pH and consequently, the zeta potential is a function of the pH. In Fig. 2 the zeta potential and the conductivity of the RBAO with 2.5 wt% of the dispersant EMPHOS CS-1361 is presented as function of the pH. The measurement was done in two steps since changing the pH influences the stearic acid coating; the first step decreasing from pH ∼6 to pH 2 and one increasing from pH ∼6 to pH 9. It was noted that above and below these pH values the RBAO starting powder starts to

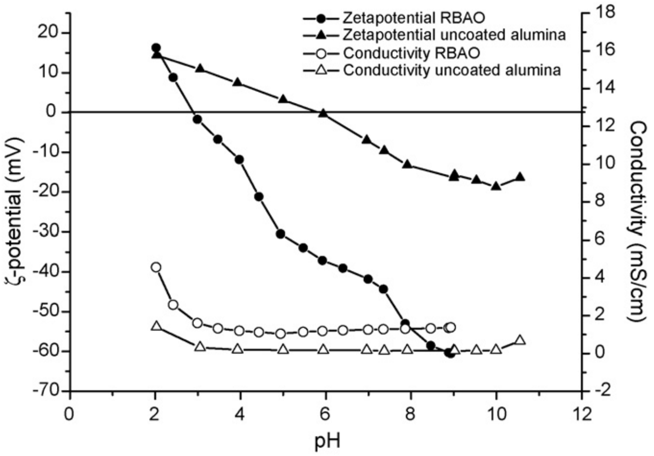

Fig. 2. Zeta potential (filled symbols) and conductivity (open symbols) of a suspension of RBAO starting powder with dispersant and unmilled uncoated alumina as function of the pH. The isoelectric point is of the RBAO starting powder was at pH 2.90, that of the alumina was at pH 5.94.

react violently. After a short time it turns white, indicating rapid oxidation of the aluminium particles.

For comparison the unmilled and uncoated alumina was measured in the same pH range. The unmilled aluminium could not be measured because of hydrolysis and, by its conductive nature, should not to contribute to the zetapotential. An effect of the alumina passivation layer on the aluminium particles can be expected though.

For this RBAO starting powder the isoelectric point (IEP) is found to be pH 2.90. Considering that the RBAO starting powder is a mixture of Al and Al_2O_3, one can compare with the zeta potential of the constituents. The IEP of alumina is was found at pH 5.84 which is lower than those found in the common values in literature of 8–9,[11–13] but the lowering of the IEP of the RBAO powder is due to the combination of dispersant and the coating. Since in the lower pH region the conductivity goes up due to the increase in ion concentration through titration by acid, the real IEP of the powder might differ a bit. For a good suspension formulation, it can be concluded that the pH is preferably higher than 5, in order to have a stable colloidal solution.

3.2. Rheological and sedimentation measurements

The first step towards an optimized suspension is to determine the optimum concentration of dispersant. Two methods have been used in order to do so: sedimentation measurements and a rheological study. In the sedimentation measurements a 25 vol% suspension of the RBAO starting powder with different amounts of dispersant was allowed to settle for 96 h after which the height of the sediment is determined. The lower the height of the sediment, the better the colloidal stability. The results are shown in Fig. 3 from which it can be seen that at a concentration of 2.5 g dispersant/100 g RBAO starting powder or more the sedimentation height remains constant.

In the rheological study the viscosity was studied as a function of the dispersant concentration. The results at a shear rate of 50 s^{-1} are shown in Fig. 3 and are consistent with the result of the sedimentation measurements. This has led to the conclusion that the optimum concentration for the dispersant is 2.5 g dispersant/100 g of RBAO starting powder.

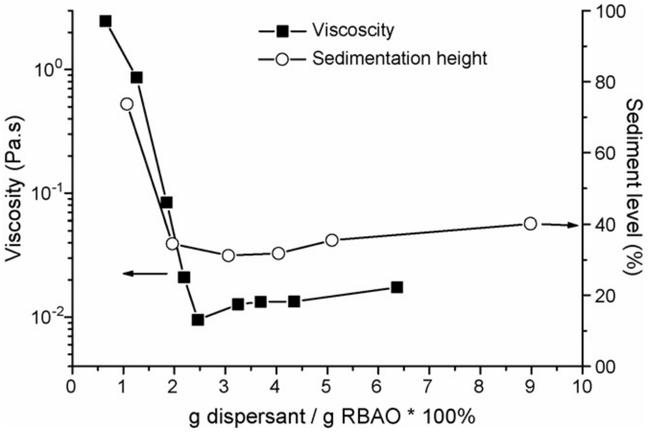

Fig. 3. Viscosity (■) and sedimentation height (○) for RBAO starting powder suspensions as function of the weight percentage of dispersant at a shear rate of 50 s^{-1}.

From the zeta potential measurements it is clear that the pH influences the particle surface charge and it is to be expected that the viscosity will be a function of the pH. In order to determine this relationship for the suspension it is important to know the influence of the pH on the separate components.

The first component tested was the RBAO starting powder. Viscosity measurements have been conducted on 25 vol% RBAO starting powder + 2.5 wt% dispersant suspensions in water at a shear rate of 50 s^{-1} at room temperature. The results are shown in Fig. 4 which shows two distinct regimes. In the pH range above 5 the viscosity is approximately constant at 0.01 Pa s. For lower pH the viscosity rises rapidly, up to two orders of magnitude.

The second component tested is the water based binder Mowilith DM765, a 50 vol% latex of polystyrene/polymethylmethacrylate (PS/PMMA), together with the plasticizer PEG400. The viscosity was measured at a shear rate of 50 s^{-1} at ambient temperature as a function of the pH. The results presented in Fig. 5 show that at $pH < 5$ the viscosity is practically constant while at $pH > 7$ the viscosity gradually rises, however

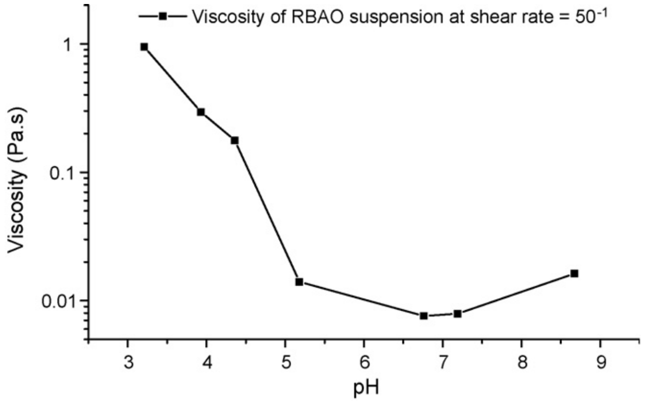

Fig. 4. Rheological behaviour of the RBAO starting powder suspension as function of the pH.

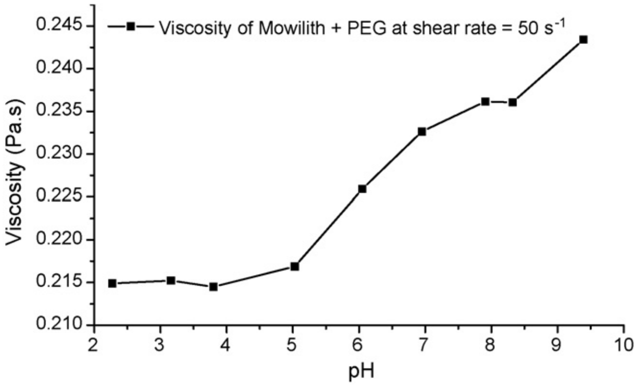

Fig. 5. Relationship between viscosity and pH for the binder system Mowilith DM 765 mixed with plasticizer PEG.

the difference in viscosity is not large. The pH of commercial Mowilith DM765 as supplied is 8–9. In Fig. 6 the relationship between the viscosity and the pH is given for the complete mixture, consisting of RBAO starting powder, dispersant, binder, plasticizer, antifoaming agent and water. The typical natural pH of the system is 6 to 7, which is close to the point with the lowest viscosity. From these results, combined with the data on the zeta potential of the RBAO starting powder, it is concluded that the pH in the range of 6 to 7 is a good choice and there is no need to add acid or base to adjust the pH.

3.3. Slurry composition

Developing a good slurry is a compromise between good green tape properties, like strength and manageability, and the final tape properties, e.g. high density and high strength. Some rules of thumb have been given by Hotza and Greil[1]: (i) the ratio between organic compounds and powder must be as low as possible; (ii) the amount of solvent must be at the minimum to maintain homogeneity; (iii) the amount of dispersant must be at a minimum; (iv) the plasticizer to binder ratio must be adjusted to obtain good green properties.

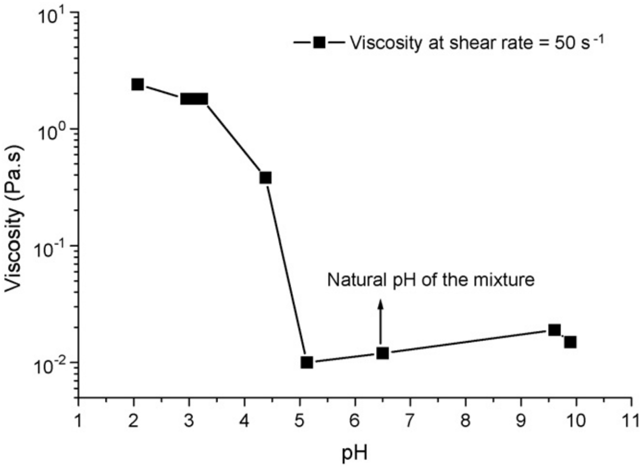

Fig. 6. Relationship for the viscosity as function of the pH of the complete mixture.

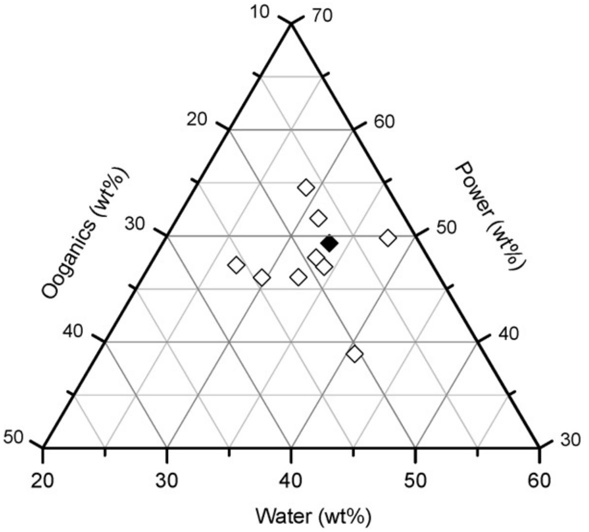

Fig. 7. Compositions of the slurry formation. The black diamond indicates the chosen slurry formation.

The various compositions tested are presented in Fig. 7. The black diamond indicates the composition giving the best results with respect to both the green tape and the sintered tapes. Suspensions higher in the diagram proved hard to tapecast due to their higher viscosity and tendency to agglomerate during tapecasting. Compositions to the right in the diagram gave poor green tapes; the tapes were cracked. The compositions lower and to the left of the black diamond in the diagram were easily to tape cast, but taking into account the rules of thumbs these were not chosen.

Compared to the slurry formation reviewed by Hotza and Greil[1] for tapecasting alumina, our chosen formation is lower in the diagram. This might be due to working with a hydrophobic RBAO powder mixture of ceramic and metallic particles, the use of a larger gap in the Doctor Blade process and the use of a different binder system; in this investigation a PS/PMMA latex binder was used, while the slurry formations described by Hotza and Greil used either cellulose or vinyl- or acrylic-type polymers.

3.4. Thermal analysis

Thermal analysis of the green tape has been performed by combined TGA/DSC measurements. The results are presented in Fig. 8. The first DSC peak at 230 °C is the combined peak of the combustion of stearic acid and PEG 400. The peaks at 264 °C, 301 °C and 410 °C are the combustion of the polymer matrix of the tape. In the temperature range of 450–600 °C the first oxidation step occurs. In this step the Al particles form a passive layer of alumina. At 662 °C the aluminium melts and starts to diffuse or break through the crust of alumina, resulting in a second oxidation in the temperature range of 750–950 °C. After this second step all the Al metal has reacted to aluminium oxide.

The TGA measurements show a minimum at ∼450 °C, the point where the combustion of the organic phase is completed.

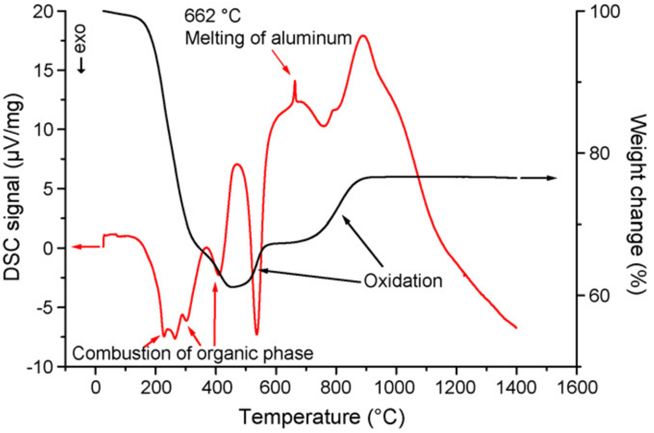

Fig. 8. TGA-DSC measurement of the tape. The heating rate was 1 °C/min in dry air.

Calculation shows that the mass loss at that point equals the mass of the organic phase in the original mixture. This indicates that no significant oxidation of the RBAO starting powder has occurred at that point. Using the mass change during the two oxidation steps, it has been calculated that 24 mass% of the aluminium metal powder has been oxidized prior to the measurement, assuming that in the original powder mixture the amount of oxidation of the aluminium powder was negligible. This oxidation can be attributed to the preparation of the RBAO starting powder.

3.5. XRD and SEM

A closer look at the various points of interest in the thermal analysis has been done by combining SEM and XRD at various temperatures: ambient temperature (25 °C); after combustion of the organic phase at 410 °C; after the first oxidation step but prior to the melting of the aluminium particles (610 °C); after the melting of Al and prior to the second oxidation step (710 °C) and after the second oxidation step (910 °C and 1100 °C). The results of the XRD are shown in Fig. 9. If one compares the peak height of alumina at ∼43° with the peak height of aluminium at ∼45°, it is easy to see that in the region up to 410 °C no oxidation takes place; the same peaks at 625 °C show a relative

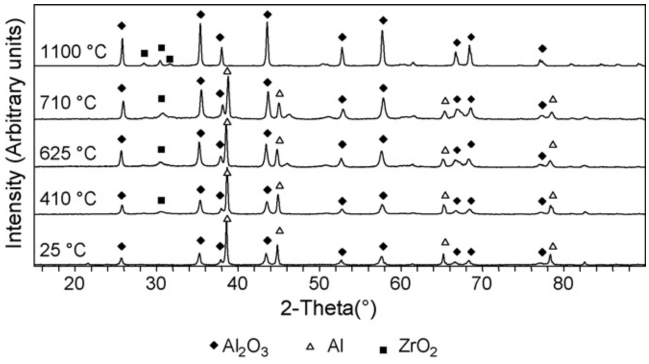

Fig. 9. XRD diagram of the powder annealed at different temperatures. The closed diamonds (◆) represent alumina; open triangles (△) represent aluminium; closed squares (■) represent the zirconia due to milling.

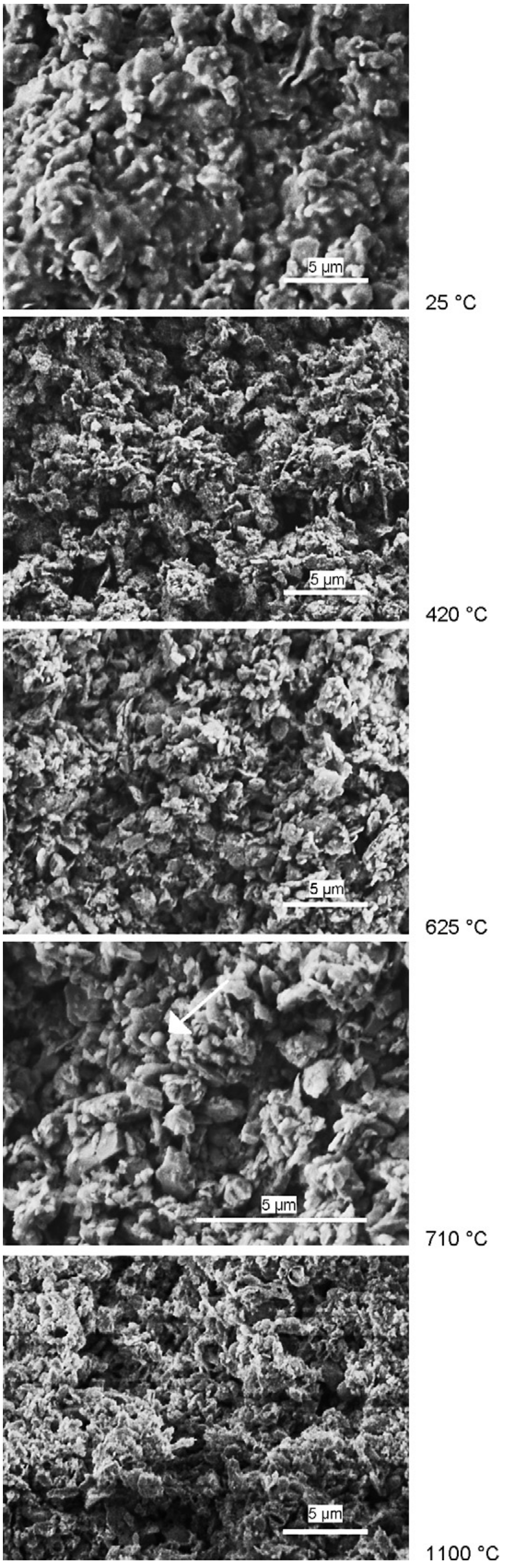

Fig. 10. Lower secondary electron image of samples annealed at different temperatures, made by SEM.

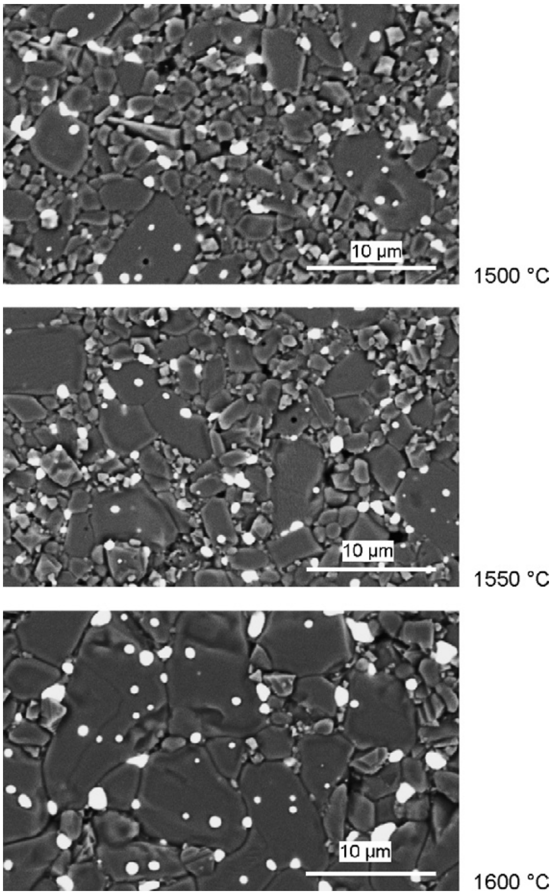

Fig. 11. Backscattered electron images of sintered and polished samples of RBAO. Samples were sintered for 4 h.

higher peak for alumina, indicating oxidation of the aluminium, with no extra oxidation occurring up till 710 °C. At 1100 °C no residual aluminium is detected. The zirconia found is due to the contamination of the mixture during milling with zirconia balls.

Samples, annealed at the various temperatures, were analyzed by SEM for comparison with the results obtained by DSC and XRD. The resulting secondary electron images are shown in Fig. 10. At 25 °C the polymer matrix is clearly visible, while from 420 °C and upwards no polymer matrix can be found. Comparing the microstructure at 420 °C and 625 °C, in between which the first oxidation step takes place, shows no discernable differences. However, at 710 °C small spherical particles, indicated by an arrow, are visible. These spherical particles are not visible at other temperatures and are most likely the result of the melting of the aluminum metal. At 1100 °C, after the second oxidation step, these spherical particles are absent and compared to lower temperature images, no substantial grain growth is discernable.

Sintered samples were analyzed by SEM using the backscatter mode to indicate possible contamination. The results are shown in Fig. 11. The grey grains are alumina particles, the clear white grains are zirconia, incorporated into the mixture due to milling with YSZ balls. The grain growth in the region 1500 °C to 1600 °C is clearly visible.

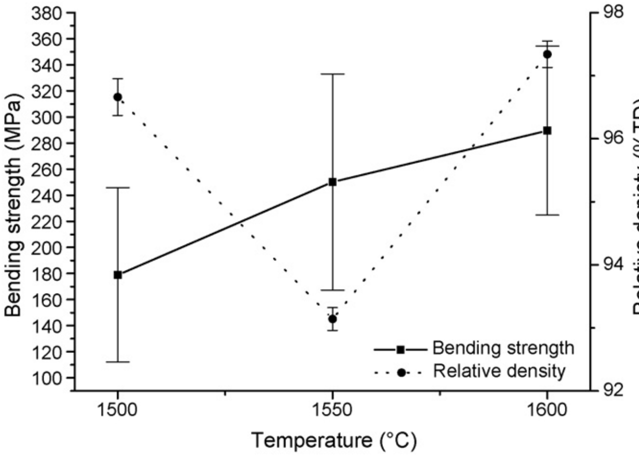

Fig. 12. The relative density as percentage of the theoretical density of alumina and bending strength in MPa as function of the sintering temperature of sintered tape.

3.6. Mechanical testing

Four point bending tests with an outer span of 30 mm and an inner span of 10 mm have been conducted on 3 samples of tapes sintered for 4 h at 1500 °C, 1550 °C and 1600 °C. The results, along with the average densities are presented in Fig. 12.

The mechanical strength increases with a higher sintering temperature. However, the density shows a minimum at 1550 °C. This can be most likely attributed to anisotropic grain growth.[14] Another possibility is the effect if liquid phase sintering. In standard available commercial alumina powder, a small amount of magnesium is added to prevent anisotropic grain growth, however, in aluminium metal powder such an addition is not common. Since the starting powder consists of aluminium and alumina, the level of magnesium is probably too low to prevent anisotropic grain growth. At 1500 °C the driving force for grain growth is probably not strong enough to induce anisotropic grain growth, but is large enough to form a intersecting network and some grain growth; at 1600 °C the driving force is large enough to induce isotropic grain growth.

The intersecting network at 1500 °C contains many defects, resulting in a low mechanical strength of 179 MPa. The anisotropic grain growth at 1550 °C gives a stronger network resulting in a higher mechanical strength of 250 MPa. Finally, sintering at 1600 °C induces isotropic grain growth, resulting in large grains with few pores and in an bending strength of 290 MPa. Compared to traditional alumina oxide with a flexural strength of 400 MPa[15] these values are low, however, it is expected that better control over the grain growth by the addition of magnesium will increase these numbers.

4. Conclusions

A powder mixture of aluminium and alumina has been successfully prepared and made hydrophobic. This opened the possibility to successful tapecasting of RBAO mixtures. After optimization of the suspension green tapes with good properties were obtained.

Thermal analysis through TGA/DSC has shown that it is possible to eliminate the organic phase prior to the start of the oxidation of the aluminium phase, enabling to obtain future ceramic-metallic composites (CMC) through tapecasting. Thermal analysis also showed that the oxidation of RBAO mixtures is a two step process; in the first step an alumina crust surrounding the aluminium particles is formed; in the second step, occurring after the melting of the aluminium, the oxidation is completed. This conclusion is supported by XRD and SEM.

Sintering the tapes showed an anomaly in the density at 1550 °C, at which a lower density was obtained then both sintering at 1500 °C and 1600 °C. This was attributed to anisotropic grain growth. In normal commercially available alumina powder a small amount of magnesium is present to prevent anisotropic grain growth, however using a mixture of aluminium, which normally has no addition of magnesium, and alumina, the level of magnesium dropped under the threshold value to prevent anisotropic grain growth.

Mechanical testing showed an increase in bending strength with a increase in sintering temperature. This was linked to the various stages of sintering in the ceramic tapes at the various temperatures.

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