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Fabrication of porous alumina ceramics from powder mixtures with sol–gel derived nanometer alumina: Effect of mixing method

A. Kritikaki [a], A. Tsetsekou [b,*]

[a] *Technical University of Crete, Department of Mineral Resources Engineering, University Campus, 34100, Chania, Greece*
[b] *National Technical University of Athens, School of Mining Engineering and Metallurgy, Iroon Polytechneiou 9, 15780, Athens, Greece*

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Abstract

This work concerns a systematic study investigating the effect on microstructure, porosity and bending strength of the addition of small amounts of very fine sol–gel derived nanoalumina on a micron-sized alumina powder for the production of highly porous ceramics. Different ways of mixing, with the nanomaterial being either in powder form (γ-alumina) or in sol state (boehmite sol), were investigated for this purpose. It was observed that when small amounts of nanomaterial (4–6 wt%) are added both the bending strength and open porosity increase to a level depending significantly on mixing method and level of dispersion of nanoparticles into the coarse matrix. The increase in strength can reach 100% in case the nanomaterial is added in powder form and 500% in case of mixing in sol state.

Keywords: Sol–gel; γ-Alumina; Nanopowder; Densification; Porosity; Bending strength

1. Introduction

Porous ceramics have attracted significant attention because of their successful use in a broad range of high value applications including filters, electronic sensors, catalysts, construction materials, etc. For most of these applications the ceramic materials need to fulfill some specific requirements regarding their microstructure, porosity, permeability, mechanical properties, etc.[1] To tailor the properties for each application, it is necessary to control the factors affecting sintering processes, such as the initial particle characteristics (e.g. particle size distribution[1–6], particle shape[7]), the microstructure,[8] the additives[6,9] and the processing technique.[9,10]

The main drawback of porous ceramics, however, is the low mechanical properties as a result of their high porosity. In order to substantially increase the strength keeping high porosity, very promising approaches are the mixing of materials with different particle size distributions and the addition of nanoparticles.[3,5,11–13] Thus, ceramics with improved mechanical properties and precisely controlled pore-structural characteristics have been developed by using bimodal powder consisting of coarse and very fine particles,[3,5,11,12] whereas many researchers are also investigating the effect of bimodal powder mixtures on final ceramic microstructure.[4,6,7] The basic assumption made is that the use of such mixtures results to better particle packing, more homogeneous microstructures, enhanced surface and grain boundary diffusion at intermediate temperatures and retarded densification at high temperatures.

The addition of aluminum hydroxide to the starting alumina powder has been also suggested in literature as a means of improving the mechanical properties (fracture toughness and bending strength) of the final porous ceramics.[10,13] These studies are exploiting the fact that $Al(OH)_3$ experiences a 60% volume contraction during decomposition producing fine Al_2O_3 grains, leading by this way during sintering to ceramics with high porosity and strong grain bonding.

Furthermore, other researchers[14–17] employed sol–gel derived monohydroxy aluminum oxide (boehmite) as a binder for extruding alumina pastes or as a dispersant[18] for slurry compaction of fine alumina powder. Their aim was not only to control the surface properties of the micron-sized powders but also to give the necessary plasticity for the processing technique. The addition of nanopowder in such form was preferred due to the fact that properties such as high purity, narrow particle size dis-

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[*] Corresponding author. Tel.: +30 210 7722213; fax: +30 210 7722119.
E-mail address: athtse@metal.ntua.gr (A. Tsetsekou).

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tribution and easy sinterability are exhibited. However, in all these studies the final goal was the sintering of ceramics in full density.

The main problems arising when a nanopowder is mixed with a micron-sized powder are related with the difficult dispersion of nanoparticles into the coarse matrix and the presence of strong agglomerates that substantially degrade the mechanical properties of final ceramics.[19,20] A novel approach to overcome the potential agglomeration of the sol–gel nanopowders and improve the dispersion of nanoparticles is to coat the coarser particles with sol[22,23] and to fabricate core–shell composites[9,24] where the coarse particles are representing the “cores” and the nanosized materials are forming “shells”. By this way, macroporous alumina ceramics with improved functional characteristics were developed at a significantly reduced sintering temperature by coating a coarse alumina powder with a titanium sulfate solution.[21] The sol coated method has also been used to coat alumina fibres with boehmite.[22] In general the core–shell method is used for coating the powders with various sintering aids and dopants aiming at lower sintering temperatures and more uniform structures.[23] This novel technique has also been employed with success for the development of porous materials with tailored porous structures and surface properties using polymer spheres as templating cores and nanosized ceramic particles as coating material.[9,24] An excellent review on the core–shell approach and its different applications has been presented by Caruso.[24]

Although there are a lot of studies investigating the production and the properties of porous ceramics with nanoparticles, the core–shell approach has been very little investigated up to now as a method to coat coarse alumina with small quantities of boehmite for developing porous ceramics. Furthermore, a comparative analysis describing the influence of different ways of mixing with the nanomaterial, in combination with the sintering conditions, on the porosity, microstructure and flexural strength is missing. In the present study different ways of mixing low amounts of very fine sol–gel derived alumina nanoparticles with a micron-sized commercial alumina were investigated for the production of ceramics with high open porosity and increased strength. The nanomaterial was added either in powder form (γ-alumina) or in the sol state (boehmite sol) to exploit the core–shell approach.

2. Experimental procedure

2.1. Development of porous ceramics

Porous alumina samples were developed by employing a commercial α-Al_2O_3 powder (Nabalox No 115-25, NABALTEC Gmbh Germany) of an average particle size of 5 μm (laser particle size distribution in Fig. 1, Mastersizer S, Malvern Instruments Ltd., UK) and a specific surface area of 1 m^2/g. The powder was mixed with 1 wt% of surfactant (Na stearate), 6 wt% of binder propyl-methoxy cellulose (DOW Chemicals, Deutschland GMbH & Co) and deionized water (20 wt%) in a shear mixer and was extruded in rods of 1 cm diameter using a piston extruder.

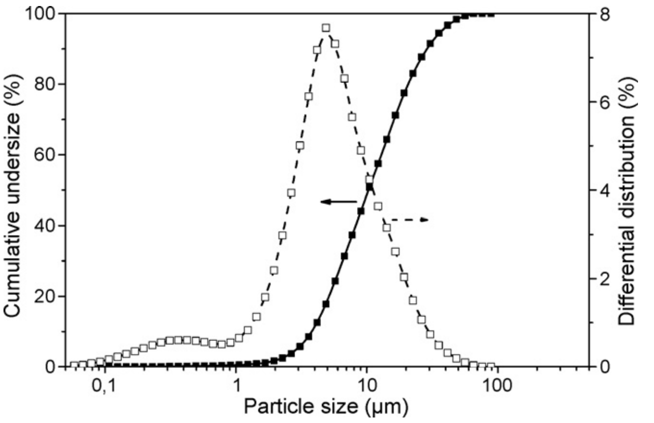

Fig. 1. Laser particle size analysis of commercial micron-sized alumina powder.

The green rods were dried at 110 °C and sintered either at 1500 °C or at 1600 °C for 2 h with a heating rate of 3 °C/min.

Exactly the same procedure was adopted to produce porous samples starting from mixtures of the commercial α-Al_2O_3 powder with sol–gel derived nanoparticles.

2.2. Preparation of mixtures of coarse alumina with sol–gel derived nanomaterial

Two different approaches were investigated in this case: mixing of the coarse powder with the nanomaterial either in powder form (γ-alumina) or in the sol state (boehmite sol). In all the cases studied, the percentage of nanoparticles added in the mixture was varied in the range 2–20 wt%. For this purpose, the quantity of sol that was mixed with the coarse powder was adjusted so that to finally receive the desired amount of nanopowder in the powder mixture during firing.

2.2.1. Mixing with the nanomaterial in powder form

In the first approach, sol–gel Al_2O_3 (γ-phase) nanopowder was synthesized using aluminum nitrate >99% ($Al(NO_3)_3 \cdot 9H_2O$) from CARLO ERBA REAGENTI as the precursor material. The aluminum nitrate was hydrolyzed in excess of water under rigorous stirring (2000 rpm, Power Control P7 Visc stirrer, IKA) and ammonia solution 25% v.v. (Riedel-de Haën) was added to catalyze the gel formation. The molar ratio employed was $Al(NO_3)_3/H_2O/NH_3 = 1/33/3.2$ with the whole reaction taking place in a batch reactor (IKA), immersed in a water-bath of constant temperature of 80 °C and ambient pressure. The produced gel was aged for 1 day at ambient temperature and then fired at 600 °C for 2 h with a heating rate of 3 °C/min. A strongly agglomerated nanopowder (HRSEM Philips XL30 FEG) with a mean particle size at around 7 nm (Philips, FEI CM20 TEM) consisting of γ-alumina phase (Philips PW 3710 X-ray diffractometer, Cu, Ka) and exhibiting a specific surface area of 174 m^2/g (B.E.T. surface area measurements on a Quantachrome Nova Series 2200 Nitrogen porosimeter) was received in this way. The as-received powder was then dry milled in a planetary mill (Pulverisette 6, Fritsch) at 180 rpm for 1 h.

The resulting nanopowder was either directly added in the shear mixer along with the commercial alumina powder and the rest of the materials (surfactant, binder, water) or it was firstly mixed with the commercial powder following a ball milling procedure to achieve a better dispersion of the nanopowder. In the latter case, the mixture of nano and commercial powder was dispersed in water (80 wt% of the powder mixture and 20 wt% of water) employing 1 wt% of surfactant (Darvan C, Vanderbilt Co, USA) and the resulting slurry was ball milled for 2 h before adding it into the shear mixer with the proper amount of the rest of polymeric additives.

2.2.2. Mixing with the nanomaterial in the sol state

In the second approach, the mixing of the nanomaterial with the conventional powder was made in the sol state. In this case, the same conditions as described above were employed for the sol–gel synthesis, however the hydrolysis was carried out in a very high water excess (molar ratio of the reactants: $Al(NO_3)_3/H_2O/NH_3 = 1/99/1.6$) to avoid the gel formation. The as-obtained sol, prior to gelation point, was mixed with the commercial powder under continuous stirring (2000 rpm, Power Control P7 Visc stirrer, IKA) and the resulting slurry after 24 h of ageing was dried at 110 °C and calcined at 400 °C in order to remove any traces of NH_4NO_3. The as-received agglomerated powder was then dry milled in a planetary mill (Pulverisette 6, Fritsch) at 180 rpm for 1 h. The resulting powder was either directly added into the shear mixer along with the proper surfactant, binder and water quantities or it was dispersed again in water employing 1 wt% of surfactant (Darvan C) and the slurry was then additionally spray dried to obtain micrometer-sized agglomerated particles. A laboratory mini spray dryer Buchi B-290 was employed for this purpose. The air inlet and outlet temperatures during the spray drying process were 150 °C and 100 °C, respectively. The viscosity of the slurries was adjusted at 2.1 mPas by the addition of 2 wt% of Darvan C (measurements performed with a Grace M3500a concentric viscosimeter at 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm and 3 rpm, at room temperature).

2.3. Characterization of developed ceramics

The open porosity and the pore size distribution of the sintered ceramics were measured by mercury porosimetry (Micromeritics Autopore IV 9400). To assume experimental reproducibility and the error of the method six of the developed ceramics, with open porosities spanned in the whole range of measured porosities, were additionally tested by performing analysis on at least five samples per case. The standard deviation in all the cases was less than 5% of the respective mean open porosity value in line with Andreola et al.[25] The microstructure was observed by HRSEM (Philips XL30 FEG). Three-point bending test measurements were performed on a Netzsch Biegefestigkeitspruefer 401 bending tester with 30 mm span and 0.5 mm/min crosshead speed. The bending strength was measured as the average of

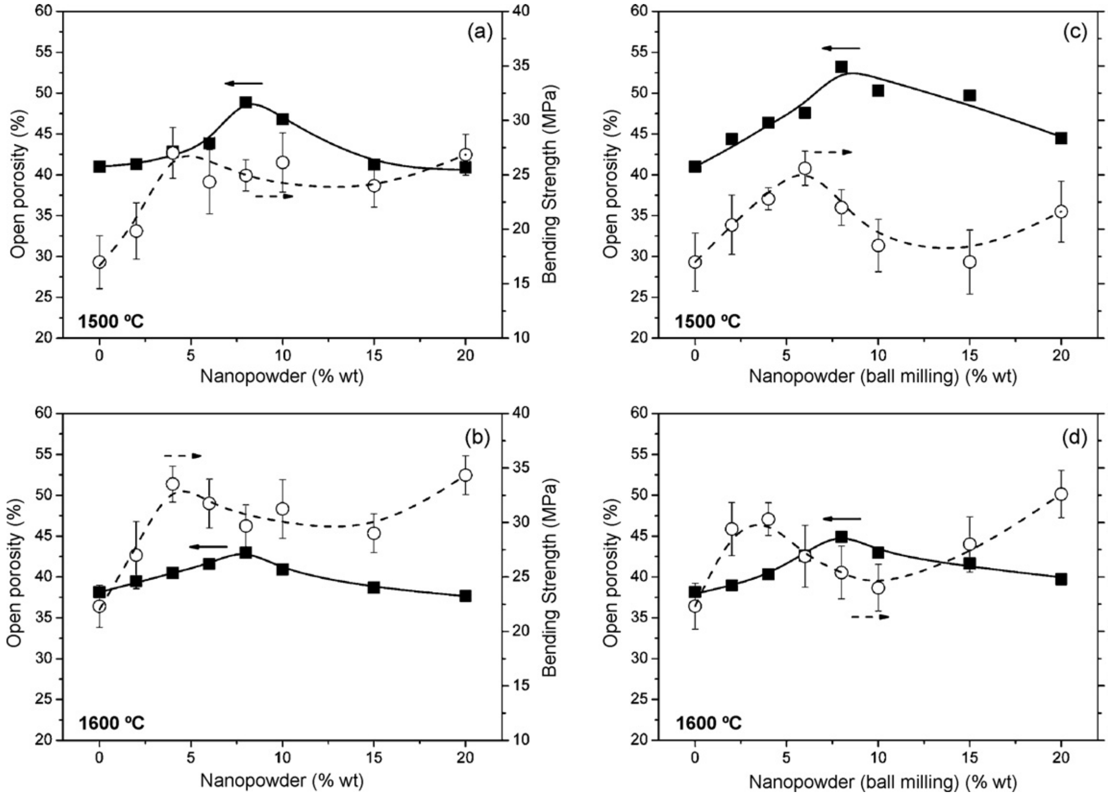

Fig. 2. Open porosity/bending strength versus the weight percentage of γ-alumina nanopowder in the powder mixture; (a) and (b) ceramics prepared by the simple mixing in the shear mixer sintered at 1500 °C and 1600 °C, respectively; (c) and (d) ceramics prepared by the addition of the ball milling step prior to shear mixing sintered at 1500 °C and 1600 °C, respectively. (■) Porosity; (○) bending strength.

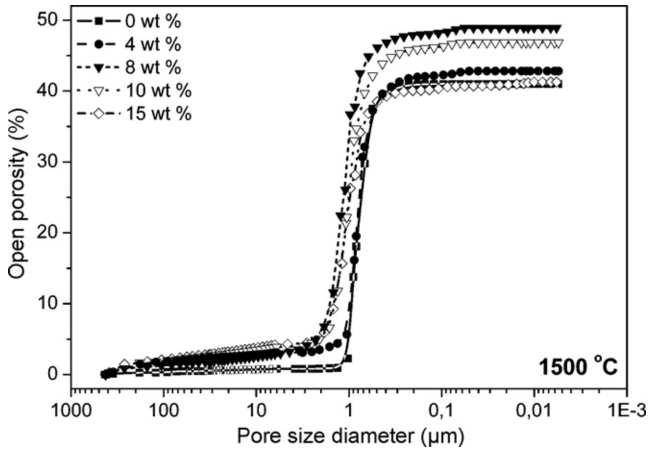

Fig. 3. Pore size distributions of alumina ceramics prepared from powder mixtures of different nanopowder content after sintering at 1500 °C. The mixing with the nanomaterial was made in powder form in the shear mixer.

15 measurements per case. The sintering behavior of the green samples was also investigated performing dilatometric studies on a Netzsch DIL 402C dilatometer. In this case the samples were heated up to 1550 °C with a constant heating rate of 5 °C/min.

3. Results and discussion

3.1. Effect of nanomaterial addition in powder form (γ-alumina)

Fig. 2 presents the open porosity and bending strength evolution versus the γ-alumina nanopowder content in the powder mixture for both mixing cases (either mixing directly in the shear mixer or ball milling preceding shear mixing, see Section 2) after sintering at 1500 °C and 1600 °C. The results indicate that the addition of nanopowder in the starting powder has as a consequence an initial increase of porosity which in all cases reaches its maximum value at a nanopowder content in the starting mixture of 8 wt%. Then as the percentage of nanopowder continues increasing, a gradual decrease of porosity is observed. This behaviour is more pronounced after firing at 1500 °C (Fig. 2a and c) and for the samples prepared from the ball-milled powder (Fig. 2c) for which the porosity increase reaches the 30%. This trend in porosity evolution is also reflected on the pore size distributions (Fig. 3) which are shifted towards higher values as the nanomaterial content in the initial powder increases up to 8 wt%, returning back when exceeding this threshold value. The maximum rise of mean pore size is also of the order of 30%.

Despite the porosity increase, the addition of nanoparticles results also in the increase of bending strength (Fig. 2) which reaches its maximum at a 4–6 wt% nanoparticles content and it is 50–70% higher (depending on the way of mixing and sintering conditions) than the respective values obtained without adding nanopowder. Thus, by adjusting the nanopowder percentage and sintering conditions ceramics with desirable properties can be obtained. For example the sample from the mixture with 4 wt% nanopowder sintered at 1600 °C shows a mean bending strength at 34 MPa at 41% porosity. This porosity value can be obtained using the pure micron-sized alumina alone after firing at 1500 °C, but the mean strength in this case is only at 17 MPa. Thus, a twofold bending strength increase at the same porosity is achieved by this way.

These results are consistent with Li et al.[11] who found a slight decrease of density and a higher increase of water absorption of sintered samples (1510 °C) shaped by isostatic pressing when they added by ball milling small percentages (up to 5 wt%) of α-nanoalumina into a mixture of micron-sized α-alumina (76 wt%) and kaolin (24 wt%). Their study showed that both the bending strength and fracture toughness increase with the nanomaterial addition reaching their maximum values (which were about 50% higher) at 2 wt% α-nanoalumina addition. Although there was no explanation for the density decrease, the strength increase was attributed to the growth of interparticle contacts due to the high diffusion rate of the nanoparticles accumulated in the grain boundaries. Li et al.[5] have also observed lower density in samples sintered at low temperature (1400 °C) when they added superfine α-alumina (10–30 wt%) to a commercial submicrometer sized α-alumina containing MgO and SiO_2 additives. They attributed this behaviour to porosity located among small grains which cannot be removed by rearrangement and solid state sintering.

Fig. 4 depicts the microstructure (under SEM) of samples prepared either without any addition of nanopowder or with 6 wt% addition after sintering at 1600 °C at various magnifications. As it can be seen, the samples without any addition of nanopowder (Fig. 4a and b) present an inhomogeneous structure and this concerns both the size and the shape of grains. The grains in this case are in their majority elongated presenting a very broad size distribution and it is very obvious that the intergrain contacts are considerably less developed. In contrast, the samples prepared by the addition of nanopowder (Fig. 4c–f) are more homogeneous consisting mainly of equiaxed grains of narrower size distribution which exhibit many and well developed contacts among them (marked with arrows). However, in this case as well, some inhomogeneities especially in grain size can be observed. In the samples prepared by the simple mixing in the shear mixer (Fig. 4c and d), large agglomerates of the initial nanoparticles, which have now been enlarged, are easily distinguished (Fig. 4c, marked in circle), whereas the samples for which the preparation procedure included the additional ball milling step (Fig. 4e–f) present some quite large grains as a result again of not optimized distribution of nanoparticles. These inhomogeneities are becoming more obvious as the nanomaterial content in the mixture increases.

These effects on microstructure and the high diffusion kinetics of nanoparticles can explain the trend on porosity and bending strength curves of Fig. 2. The presence of nanograins favor the neck formation in the early stages of sintering facilitating by this way the growth of intergrain contacts and resulting earlier to larger (and finally to more equiaxed) grains that retard densification during the last sintering stages. A much stronger grain bonding should be also developed in this case in accordance with Deng et al.[10] As a consequence both strength and

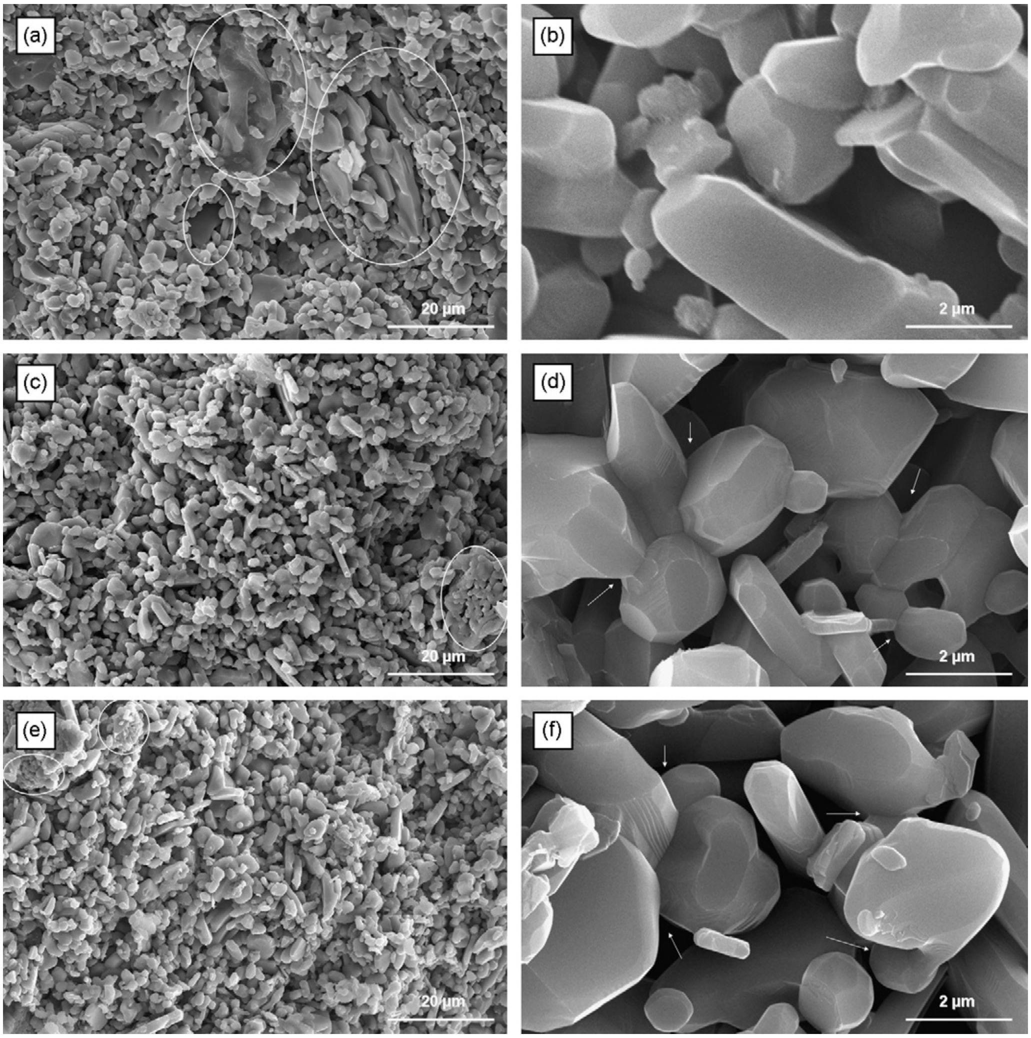

Fig. 4. SEM pictures of alumina ceramics sintered at 1600 °C; (a) and (b) alumina ceramics prepared from pure micron-sized alumina powder without nanomaterial addition; (c)–(f) alumina ceramics prepared from mixtures containing 6 wt% nanoparticles made with the nanomaterial in powder form (γ-alumina): (c) and (d) ceramics prepared using the simple mixing in the shear mixer, (e) and (f) ceramics prepared by mixing in powder form followed by ball milling prior to shear mixing. Circles mark large inhomogeneities. Arrows point out grain contacts.

porosity initially increase with the addition of small amount of nanomaterials.

This would ideally occur in case that a complete coverage of surface of the coarse alumina particles by the nanograins could be achieved. However, as the nanomaterial percentage continues increasing above the threshold value, which was measured at around 8 wt% in our case, the combination of faster sintering kinetics and of better packing of particles results in the gradual decrease of porosity in consistency with literature results.[3,4,6,7,16] The better packing in case of bimodal distributions has been long discussed and an optimum packing at a fine powder content at around 20–30 wt% is reported[3,5–7,12,16–18] attributed to the filling of voids among the coarse particles with the small ones. It becomes obvious that the homogeneity has to play an important role in this combined phenomenon of both porosity and strength increase, because as the nanoparticles form large agglomerates, these would concentrate on the voids of coarse particles (even for low nanomaterial addition) and the effect on porosity increase would be less pronounced from the beginning. This could explain the higher porosity values observed in the case of the ball-milled powders. However, the further inclusion of this extra ball milling step adds effort without offering significant improvements both in terms of dispersion and properties.

This trend in porosity is also reflected on bending strength, which after its initial increase starts decreasing slowly with the further porosity increase presenting a local maximum. The already mentioned increased inhomogeneity with the nanomaterial content due to strong agglomeration of nanopowder can also affect the further strength rise. Deng et al.[19,20] have recognized that a uniform microstructure without strong agglomerates in the green compacts of ZrO_2 with nano-additions is the key to obtaining high strength porous ceramics. But, then again, as the porosity starts decreasing, the strength shows a second continuous rising as the nanomaterial content increases, a phenomenon which has been observed many times in literature attributed

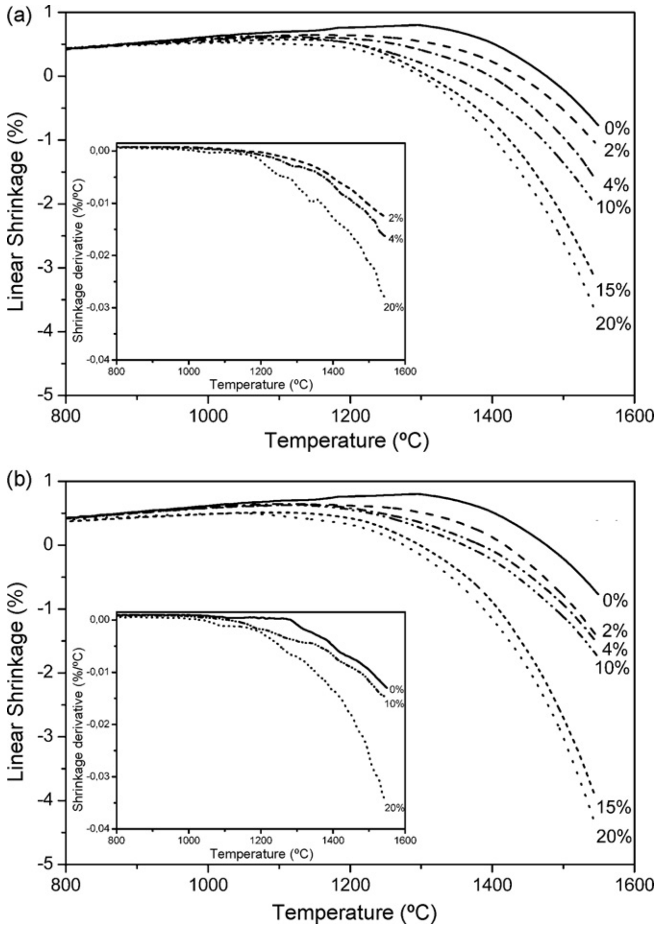

Fig. 5. Dilatometric curves versus firing temperature on powder mixtures of coarse powder with γ-alumina nanopowder prepared by: (a) simple mixing in the shear mixer; (b) adding the extra ball milling step prior to shear mixing. The numbers besides the curves show the respective nanopowder wt% in the mixture.

also to faster diffusion kinetics of nanomatter which facilitate neck growth at low sintering temperatures strengthening grain bonding.[3,6,10,13]

The behaviour of the powder mixtures during sintering was also investigated through dilatometric studies. The results confirmed the assumption of faster kinetics during the initial sintering stages. In Fig. 5a and b, it can be easily seen that as the nanopowder content increases the shrinkage curves are shifted towards lower temperatures and become more abrupt. According to literature the γ-alumina nanopowder at first transforms to θ-alumina and then to α alumina, at around 1100 °C, through a nucleation and growth process which results in significant volume shrinkage and grains rearrangement, leading, by this way, to a very abrupt shrinkage at the transformation temperature.[8] However, in our case, although there is a significant shift of the shrinkage start towards lower temperature, the shrinkage continues smoothly up to the whole temperature range with perhaps the exception of the samples with 20 wt% and much less with 15 wt% nanopowder addition, for which this shrinkage phenomenon at around 1100 °C becomes distinguishable, reflected also on a small peak in the first derivative of shrinkage curve. The reason for not clearly observing this abrupt phenomenon is the low nanopowder content and the high space volume which permits the transformed α-alumina to be rearranged without any abrupt volume shrinkage. Again, not any significant difference could be observed between the samples prepared with or without the extra ball milling step.

3.2. Effect of nanomaterial addition in the sol state

Fig. 6 presents the open porosity and bending strength in correlation with the nanoparticle content in starting mixture for both mixing cases examined when the nanomaterial was added in the sol state (either direct use of calcined powder mixture into the shear mixer or redispersion in water and spray drying before shear mixing, see Section 2). As it can be seen the porosity rises considerably by adding small quantities of nanomatter. The maximum values in porosity curves were obtained at around 8–10 wt% nanomaterial content. The highest porosity was achieved by the simple mixing and firing at 1500 °C (Fig. 6a) and it was 36% higher than the value obtained without any nanomaterial addition. A similar rate of increase but lower porosity values in the whole spectrum of nanomaterial addition percentage were obtained after firing at the same temperature (1500 °C) when the extra spray drying step was added (Fig. 6c). In contrast, a very steep porosity rise with the nanomaterial content (81% final increase) was observed in this case, for sintering at 1600 °C (Fig. 6d) reaching finally the same maximum as in the case of simple mixing (Fig. 6b).

However, although there is a considerable increase of porosity, the bending strength is increasing too reaching very high values. For both mixing procedures (with or without the addition of the spray drying step) the increase of strength is of the order of 400–500%. This is consistent with Kwon and Messing[3] who have also showed that ceramics prepared by a coarse alumina/boehmite mixture could increase their mechanical strength by 2–4 times relatively to samples coming from the coarse alumina powder alone. But, in their case, this occurred through the addition of a high percentage of nanomaterial which was ranged between 30 wt% and 70 wt%.

In Fig. 7a–d the microstructure examination of the sintered ceramics containing 6 wt% nanoparticles is presented. In the case of adding the spray drying step in the whole procedure (Fig. 7c and d), the homogeneity of microstructure is almost perfect and a very uniform grain size distribution is presented as a result of the very good dispersion of nanoparticles into the main matrix. A less homogeneous structure is revealed, however, in the case of not including the spray drying step (Fig. 7a and b). In the relevant samples, some irregular grain growth (marked in circle), attributed to the presence of some agglomerates developed in the powder mixture, could be observed among the rest of the structure which was appeared very homogeneous, consisting of grains with a narrow size distribution.

The very good nanomaterial dispersion achieved through the spray drying step is reflected on the sintering behaviour of samples. The respective samples exhibit very fast sintering kinetics in the early stages of sintering and this is depicted in the shrinkage curves obtained in the dilatometer (Fig. 8b). The shrinkage curves in this case are shifted towards lower temperature

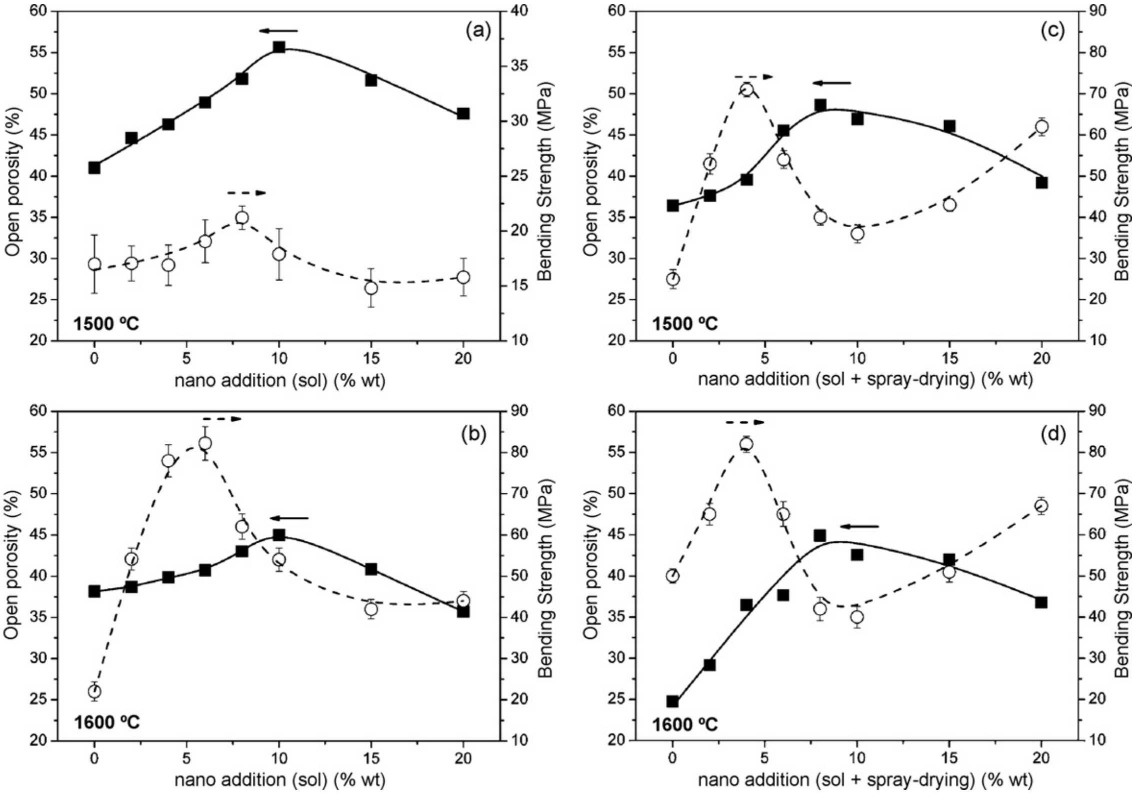

Fig. 6. Open porosity/bending strength versus the weight percentage of nanoparticles in the powder mixture; (a) and (b) ceramics prepared by the simple mixing with the boehmite sol sintered at 1500 °C and 1600 °C, respectively; (c) and (d) ceramics prepared by the addition of the spray drying step prior to shear mixing sintered at 1500 °C and 1600 °C, respectively. (■) Porosity; (○) bending strength.

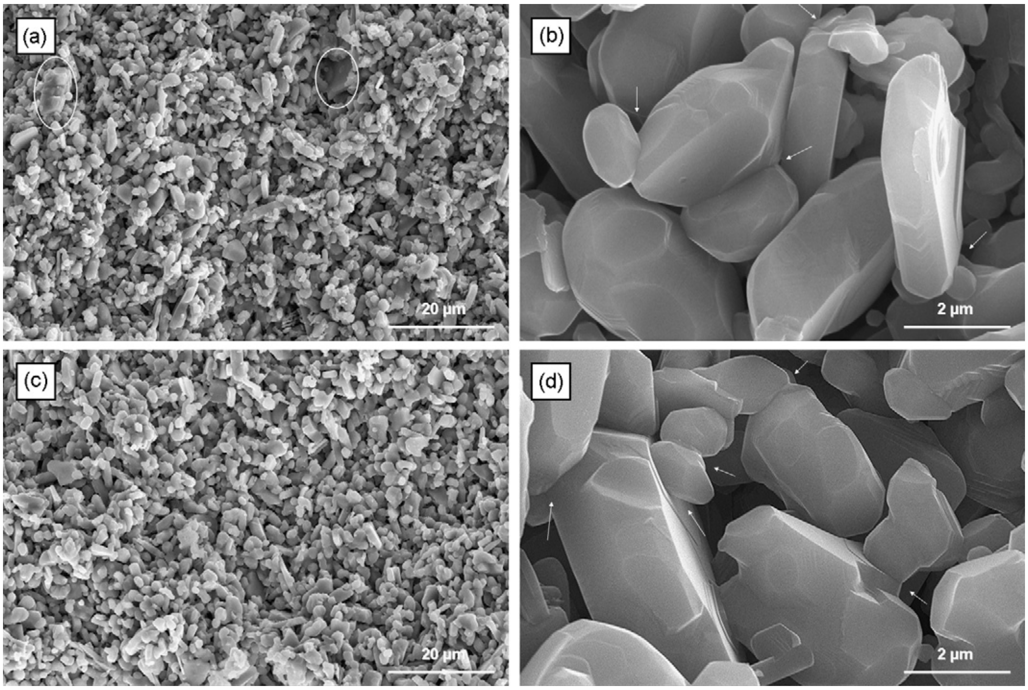

Fig. 7. SEM pictures of alumina ceramics prepared from mixtures containing 6 wt% nanoparticles made with the nanomaterial in the sol state (boehmite) sintered at 1600 °C; (a) and (b) ceramics prepared using the simple mixing in the sol state; (c) and (d) ceramics prepared by mixing in the sol state followed by spray drying. Circles mark irregular grain growth. Arrows point out grain contacts.

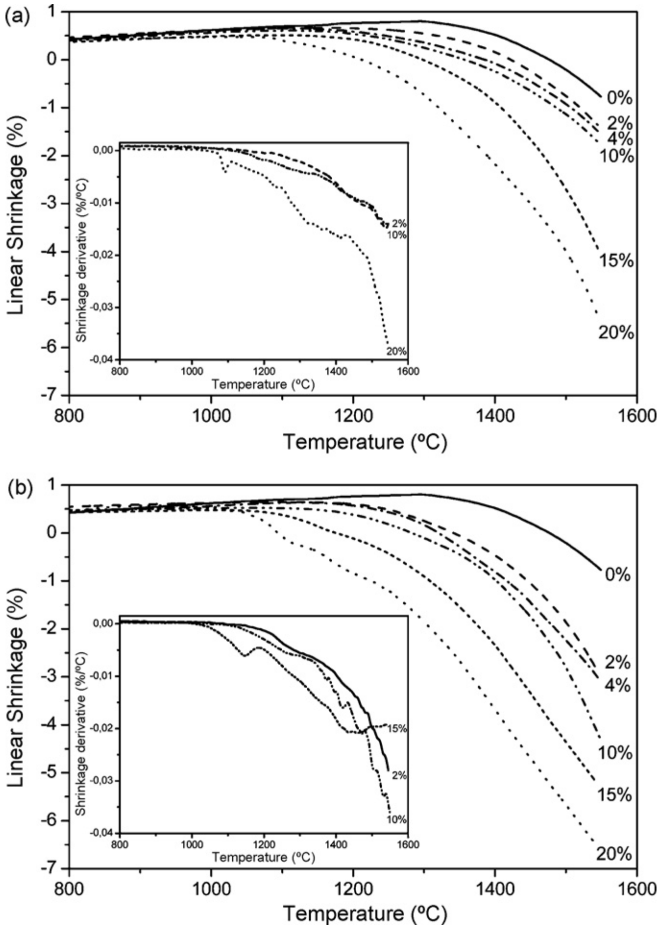

Fig. 8. Dilatometric curves versus firing temperature on powder mixtures made with the nanomaterial in sol state (boehmite); (a) simple mixing with boehmite sol; (b) mixing with boehmite sol followed with the extra spray drying step prior to shear mixing. The numbers besides the curves show the respective nanopowder percentage in the mixture.

values and become more abrupt, when compared to the curves obtained from the respective samples prepared without spray drying (Fig. 8a). However, both kinds of samples prepared by mixing in the sol state showed higher diffusion kinetics compared to the respective samples for which the nanomaterial was mixed in powder form. Furthermore it was seen that, as in Section 3.1, the higher the nanomaterial content in the starting powder mixture is, the more the shift of the shrinkage curve towards lower temperatures.

The faster kinetics observed here come as a result of better packing and more uniform dispersion of the nanomaterial when mixed in the sol-state, since in this case the coarse alumina is coated with the boehmite sol developing a core–shell structure.[24] This microstructure can be seen in powder samples prepared by both sol-mixing procedures with and without spray drying after mixing (Fig. 9a and b). It is obvious that the coating of the micron-sized alumina grains with the nanomaterial affects considerably their behaviour as it provides them with the exceptional characteristics of the nanomatter (fast diffusion kinetics) while keeping their initial characteristics.

The consequence of this behaviour is the final porosity evolution already discussed in Section 3.1 and described earlier in this section. Exactly the same trend in the curves is also presented here, for the case of mixing in the sol state, with the maximum appearing at almost the same nanomaterial addition (8–10 wt%) as in the previous section. However, the effect on porosity is even more pronounced for mixing in the sol state as a result of the better dispersion and this is especially true for the samples prepared from the better dispersed spray dried powder mixtures. This is reflected on bending strength, which shows exactly the same behaviour discussed in Section 3.1. But, here, the increase in strength is spectacular and especially in the case of including the spray drying process. Thus, by this way, a sample with a 45% porosity and a bending strength of 71 MPa can be produced, which otherwise would have a bending strength less than 17 MPa (the mean strength measured in the samples from the pure micron-sized alumina for which the porosity obtained is 41%).

The densification kinetics in the case of mixing in the sol state but without being followed by spray drying, are slower resulting in higher porosity values at 1500 °C and thus the strength increase after firing at this temperature is not so impressive. However, as the sintering temperature increases to 1600 °C and the porosity values are decreased, the bending strength shows again this impressive rise leading to ceramics exhibiting a mean bending strength of the order of 82 MPa at a porosity of 41%. Thus an almost fivefold strength increase was achieved compared to the samples of the same porosity prepared from the pure micron-sized alumina powder. A similar combination of

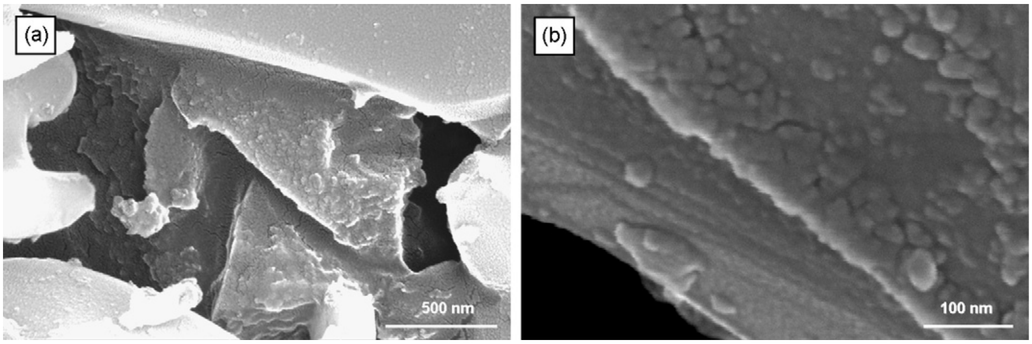

Fig. 9. Details of alumina powder grains under SEM showing their coverage by a nanoparticle layer; (a) simple mixing in sol state; (b) mixing in sol state followed by spray drying.

properties can be also obtained with the spray drying procedure. However, the very positive results obtained for the samples prepared without spray drying the powder mixture after sintering at 1600 °C suggest that the spray drying step can be omitted although it offers perfectly homogenized microstructures.

The difference in behaviour between the samples prepared with and without spray drying can be attributed to the better particle packing in case of spray drying. This has as an effect the parallel shift of the whole porosity curve obtained after sintering at 1500 °C to lower values for the entire range of nanomaterial addition examined, including the samples made from the pure micron-size powder (0 wt% nanocontent) after its spray drying. Furthermore, at 1600 °C, despite the fact that the sample without nanomaterial is denser in case of spray drying, the maximum porosity obtained for both methods with and without spray drying is similar as a more pronounced effect of nanomaterial content on porosity is observed for the samples made from spray dried powders as already discussed.

4. Conclusions

Porous ceramics were fabricated from powder mixtures of a micron-sized alumina powder with small amounts (2–20 wt%) of sol–gel derived nanoalumina. Different ways of mixing the powders were investigated with the nanomaterial being added either in powder form or in the sol state.

It was shown that the addition of small amounts of nanomaterial (4–6 wt%) leads to increase of both the open porosity and the bending strength. This effect is more pronounced as the dispersion of nanoparticles into the coarse alumina matrix is improved suggesting the powders mixing method as a very important parameter. Thus, ceramics prepared employing the nanomaterial in powder form exhibit less uniform microstructure showing a bending strength increase up to 100%. The addition of an extra ball milling step cannot improve significantly the results. However, when the nanomaterial is added in the sol state, the microstructure is very uniform, especially in the case of including an extra spray drying step after powder mixing, and the increase in bending strength can reach the 500%.

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