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Journal of the European Ceramic Society 26 (2006) 3133–3138

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Synthesis of zirconia–alumina and alumina–zirconia core–shell particles via a heterocoagulation mechanism

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Received 3 June 2005; received in revised form 12 August 2005; accepted 22 August 2005
Available online 24 October 2005

Abstract

This study describes the synthesis of core–shell particles, consisting of a ZrO_2 or Al_2O_3 submicron nucleus coated by a nanolayer of Al_2O_3 or ZrO_2, respectively. The oxide layers around the cores are deposited via a heterocoagulation route, based on the attraction of oppositely charged core and shell particles.

TEM micrographs clearly show a homogeneous Al_2O_3 shell (originating from boehmite or γ-Al_2O_3 particles) around the ZrO_2 cores and in the other case, a ZrO_2 layer (originating from hydrothermally prepared ZrO_2) around the submicron Al_2O_3 cores. From PCS measurements, it can also be deduced that the cores are enwrapped by a shell and it is calculated that the thickness of the Al_2O_3 shell is about 30–35 nm and the ZrO_2 layer is approximately 80 nm. The coated powders are additionally characterized by XRD.

Keywords: Composites; Electron microscopy; Al_2O_3; ZrO_2; Heterocoagulation; Coated particles

1. Introduction

Composite particles consisting of a core coated with another compound have received considerable interest because of the promising technological applications of such systems. Coatings are applied for changing the surface characteristics of a powder and consequently to improve for instance the dispersability, the thermal stability or the magnetic properties.[1–6]

Most literature reports deal with the coating of metals,[7,8] carbides[1,9] or polymers,[5,10–12] but recently some oxide materials are coated as well.[13,14] In this study, oxide–oxide composites, in particular ZrO_2–Al_2O_3 and Al_2O_3–ZrO_2 core–shell particles, are synthesized. These core–shell particles will be used in ceramic composites, i.e. sintered pellets of ceramics consisting of a matrix phase in which a second phase is incorporated. Sintered ceramic composites with an Al_2O_3 matrix and ZrO_2 as a second phase, have already been synthesized in our laboratory.[15] For comparison, ZrO_2–Al_2O_3 core–shell particles (i.e. a shell consisting of the matrix phase) will be incorporated as a second phase in the alumina matrix to study the effect on its grain growth and its mechanical properties.

Several methods can be used to deposit surface coatings on particles. The mechanofusion process[10,16] is based on intensive mixing and compression of the raw particles, resulting in strong mechanical forces generating thermal energy. Owing to this energy and to the difference in melting temperatures, the shell particles will fuse with the surface of the core particles. With this technique, it is possible to obtain a very homogeneous shell around the core. However, for ceramic materials a lot of energy is needed because of their very high melting temperatures.

The most commonly used technique for powder coating is heterogeneous nucleation.[1,3,9,17,18] When preparing oxides, the cores are dispersed in solutions of the predestinate coating material, which will precipitate as a metal hydroxide on the surface of the cores upon changing the pH of the solution. After calcining, the shell is transformed into an oxide layer. Nevertheless, it is difficult to avoid homogeneous nucleation when using this technique.

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0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.08.015

In this study, the different powders are coated via a heterocoagulation approach.[19,20] This technique can be used for powders which have a sufficiently different isoelectric point. The pH can then be chosen in such a way that the powders have an opposite charge and the particles undergo electrostatically driven coagulation. In general, the core is a rather large particle and the shell consists of smaller particles. Ideally, a continuous monolayer of the small particles will attach to the surface of the core, resulting in a homogeneous layer after thermal treatment.

2. Experimental details

2.1. “Core” materials

Yttrium stabilised ZrO_2 (YSZ) (TZ-3Y, TOSOH, approximately 300 nm) and α-Al_2O_3 (AKP-30, Sumitomo, approximately 500 nm) were used as core materials.

Aqueous suspensions of 0.2 vol.% YSZ or α-Al_2O_3 powder were prepared which were ultrasonically treated prior to coating. Henceforth, these cores will be named YSZ or alumina cores.

2.2. “Shell” materials around YSZ cores

2.2.1. γ-Al_2O_3 particles as shell material

On one hand, an aqueous solution (2 vol.%) of commercial γ-Al_2O_3 (Baikalox CR125, Baikowski, about 20 nm) was prepared and ultrasonically treated in order to coat the YSZ cores.

2.2.2. Boehmite particles as shell material

On the other hand, the YSZ cores were coated with boehmite, which was synthesized via the Yoldas method.[21] After the synthesis, a sol of boehmite particles was obtained, which was used as such in the coating procedure.

2.3. “Shell” material around alumina cores

The shell around the alumina cores is composed of 3Y-ZrO_2 nanoparticles, which were hydrothermally prepared. The hydrothermal procedure is based on the method of Denkewicz et al.,[22] but several adjustments are made.

First, an aqueous solution (0.25 M) of $ZrO(NO_3)_2 \cdot xH_2O$ (zirconyl nitrate hydrate, 99.9%, Aldrich) was prepared. A stoechiometric amount of $Y(NO_3)_3 \cdot 6H_2O$ (yttrium(III) nitrate hexahydrate, +99%, Merck) was added, according to the ratio 3 mol% Y:97 mol% Zr. After stirring for 30 min, a diluted solution of NH_3 (Aldrich; 4.98 N) was slowly added until the pH reached a value of 7.3. Under the present conditions, both metal ions are present as hydroxides, forming a gelly precipitate. This precipitate was filtered and repeatedly washed with water to remove remaining nitrates. Thus, the obtained washed precipitate was put into a Teflon-lined Parr® pressure-vessel together with water (70 ml), and hydrothermally treated in an oven at 200 °C for 2 h. After the hydrothermal treatment a suspension of 3Y-ZrO_2 particles was obtained.

2.4. Coating via heterocoagulation

ζ-potential measurements (Delsa™ 440SX Zeta Potential Analyzer, Beckman Coulter) were carried out (in KCl; 0.01 M) on the suspensions of the starting powders as a function of the pH to determine the isoelectric points of the separate materials.

The suspensions of the core powder and the shell powder are mixed together. The pH of the resulting suspension was then adjusted with aqueous ammonia (Aldrich, 4.98 N) to a value between the isoelectric points of the starting products. Subsequently, this suspension was stirred at 60 °C for one night, then filtered (membrane filter 0.1 μm, Pall) and dried at 60 °C.

The dry powders were calcined in a tube oven in order to form a homogeneous shell of the desired oxide phase. The coated powders with an alumina core were calcined at 700 °C for 1 h, whereas the coated YSZ cores were calcined at 800 °C during 2 h in order to form the desired crystallographic phase.

2.5. Characterization techniques

Suspensions of the core materials, the shell materials and the coated powders were measured by photon correlation spectroscopy (PCS, ZetaPALS with BI-MAS particle sizing option, Brookhaven Instruments Corporation) in order to determine the particle size distribution. Although it is known that the calculation of the mean particle diameter by means of PCS is based on a model in which the particles need to have a spherical shape (which is not always completely correct for the powders in this study), this technique was still used to have a notion about the sizes.

Furthermore, the coated powders were characterized by powder X-ray diffraction (XRD) using a Siemens D-5000 diffractometer (Cu Kα_1 radiation). Transmission electron microscopy (TEM) pictures were made on a Philips CM12. The elemental composition was simultaneously determined by means of energy dispersive X-ray spectrometry (EDX).

3. Results and discussion

3.1. Isoelectric point determination of the starting powders

For determining the isoelectric point, a ζ-potential–pH curve was measured for all the suspensions, consisting of the separate starting powders. In Table 1 the isoelectric points of the starting materials are summarized. The positions of the isoelectric

Table 1
The measured isoelectric points of the starting powders

Material	Isoelectric point
Core	
3Y-ZrO_2 (YSZ/TOSOH)	±5.4
α-Al_2O_3 (alumina/AKP-30)	±8.7
Shell	
γ-Al_2O_3 (Baikowski)	±8.0
Boehmite (Yoldas)	±9.8
3Y-ZrO_2 (hydrothermal)	±6.3

points of alumina and zirconia correspond well with literature values.

The powders containing aluminium have a rather high isoelectric point, in contrast with ZrO_2. At a pH lower than the isoelectric point, the ζ-potential is positive. Upwards of the isoelectric point, it is the opposite; meaning that the shear plane is negatively charged. For materials with sufficiently different isoelectric points, which is the case for alumina and zirconia, it is possible to coat these materials on one another via heterocoagulation at a pH between the isoelectric points.

3.2. Coating of YSZ cores with γ-Al_2O_3

The pH region for the heterocoagulation process to take place can be roughly determined between 5.5 and 8 on the basis of the ζ-potential curves of YSZ and γ-Al_2O_3 (Fig. 1a). In this domain, the ZrO_2 core is negatively charged, whereas the Al_2O_3 shell particles are positively charged. The coating process was carried out at an intermediate pH of 6.6.

According to PCS, the mean particle diameter of the uncoated YSZ core at pH 6.6, at which the coating will take place, is about 210 nm. The primary particle size (before the coating process) of the γ-Al_2O_3 shell material, is about 20 nm – as seen by TEM –, but at pH 6.6 these particles are quite strongly agglomerated. Here, the mean particle diameter as determined by PCS is around 335 nm.

In this case, the most suitable quantity of shell material was about two times (in molar ratio) the amount of core material. When less γ-Al_2O_3 was used, the cores were not completely covered, i.e. there was a lot of free place on the core which was not occupied by a shell. On the other hand, using more shell material, there was a lot of superfluous γ-Al_2O_3, which was not bonded at the core.

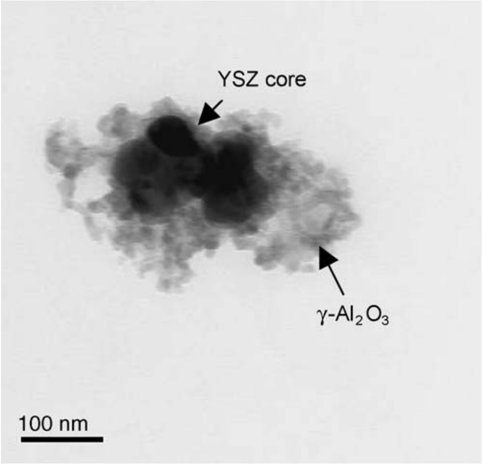

Fig. 2. TEM-photo of a YSZ core coated with γ-Al_2O_3, calcined at 800 °C for 2 h. This picture is representative for the full sample.

A TEM-image (Fig. 2), with an additional EDX-analysis, of the coated and calcined powder clearly shows that the YSZ core is completely covered with a γ-Al_2O_3 shell. Besides that, a ζ-potential curve of the coated and calcined powder (Fig. 1b) also proved that the YSZ core was covered with γ-Al_2O_3, because the isoelectric point of this powder is close to that of the original shell material.

The coated and calcined powder was also measured by means of PCS. The mean particle diameter after coating was considerably increased in comparison with the diameter of the uncoated powder, indicating that the core was covered by a shell. Out of the difference between the diameter of the coated and the uncoated

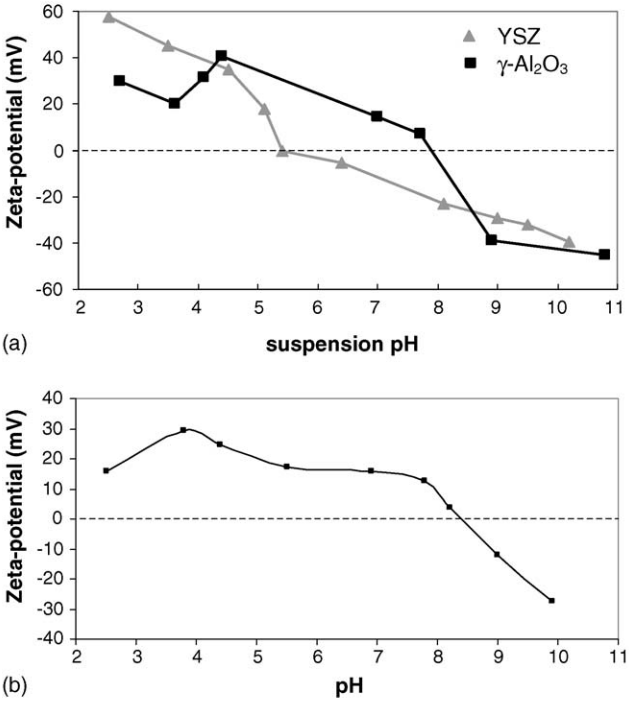

Fig. 1. (a) ζ-potential curves of YSZ and commercial γ-Al_2O_3. (b) ζ-potential curve after coating and calcining (2 h at 800 °C).

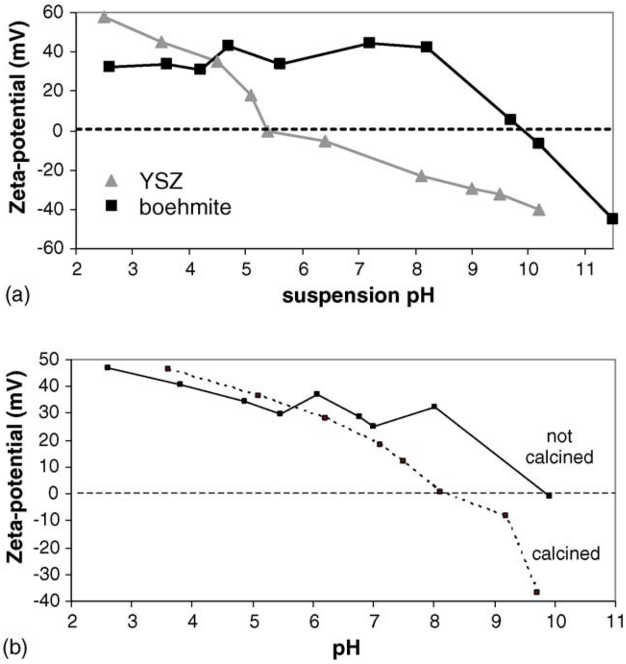

Fig. 3. (a) ζ-potential curves of YSZ and boehmite. (b) ζ-potential curves after coating; (_) not calcined, (. . .) calcined at 800 °C for 2 h.

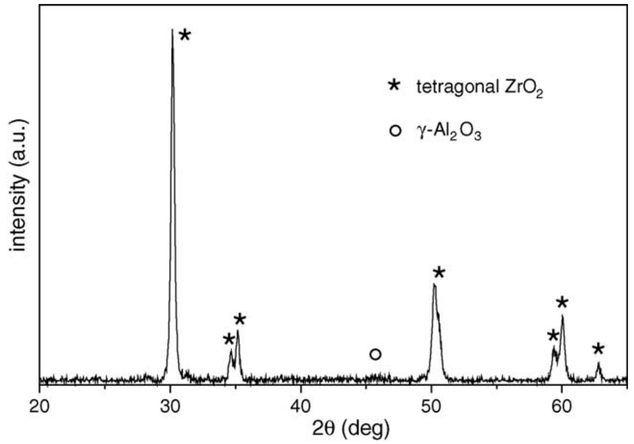

Fig. 4. XRD-spectrum of the YSZ core coated with boehmite particles, calcined at 800 °C for 2 h.

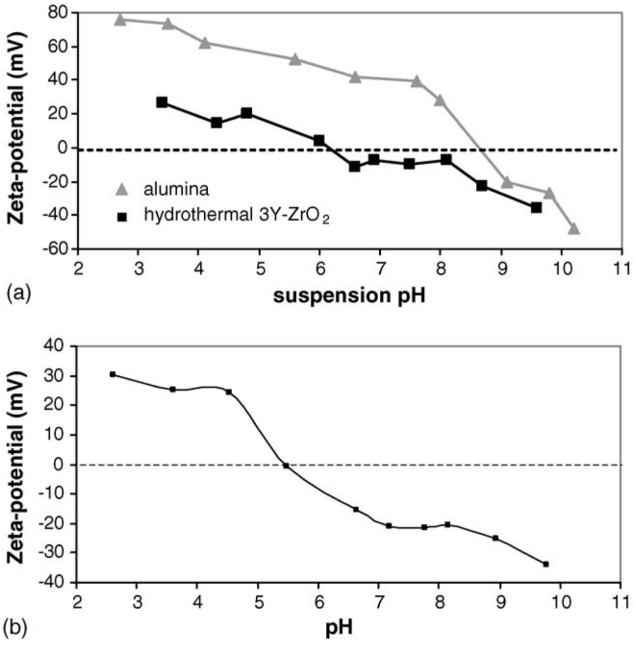

Fig. 6. (a) ζ-potential curves of alumina and hydrothermally prepared 3Y-ZrO_2. (b) ζ-potential curve after coating and calcining (1 h at 700 °C).

powder, it could be deduced that the mean layer thickness of γ-Al_2O_3 is around 35 nm.

Everything goes to show that it was possible to cover the YSZ core with γ-Al_2O_3 particles at pH 6.6, in spite of the agglomerated state of the γ-Al_2O_3 particles before coating.

3.3. Coating of YSZ cores with boehmite

In Fig. 3a, the ζ-potential curves of the YSZ core suspension and the Yoldas sol of boehmite particles are presented. The coating of the YSZ cores with boehmite particles can be performed in a rather wide pH range between 5.5 and 10. An intermediate pH of 7.3 was chosen for the coating process because at this point the difference between the surface charges is the largest, providing an easier electrostatic attraction.

The particle diameters of the core and the shell material and their state of agglomeration before coating were simultaneously characterized via TEM and PCS. According to PCS-results, the mean particle diameter of the uncoated YSZ core at pH 7.3, at which the coating will take place, is about 290 nm. The boehmite particles have a primary particle size of more or less 20 nm, as concluded from TEM-analysis. With PCS, a mean diameter of about 50 nm at pH 7.3 was found, so it can be concluded that the boehmite particles are quite well dispersed at the coating pH.

In this coating process, the optimal amount of shell material is four times the amount of core material (in molar ratio) to obtain a homogeneous coating and no surplus of shell material.

After the coating process, the powder was calcined in order to convert the boehmite particles into an oxide (in this case γ-Al_2O_3). In the XRD pattern (Fig. 4), it can be clearly seen that

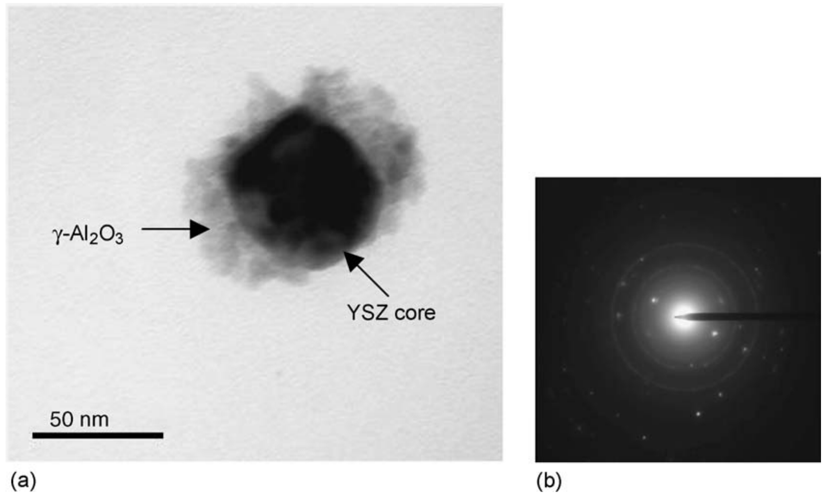

Fig. 5. TEM-image (a) and electron diffraction pattern (b) of the YSZ core coated with boehmite particles, calcined at 800 °C for 2 h. All the coated particles are similar to the one shown.

there are no diffraction peaks of boehmite anymore. The diffraction peaks of γ-Al_2O_3 are difficult to distinguish from the noise because of its semicrystalline nature which is due to the high number of defects.

A TEM-image (Fig. 5a) of the coated and calcined powder demonstrates that a nanolayer surrounds the core well. From the dots in the electron diffraction pattern (Fig. 5b), it can be concluded that the core is composed of tetragonal ZrO_2. The rings are representative of the γ-Al_2O_3 shell material.

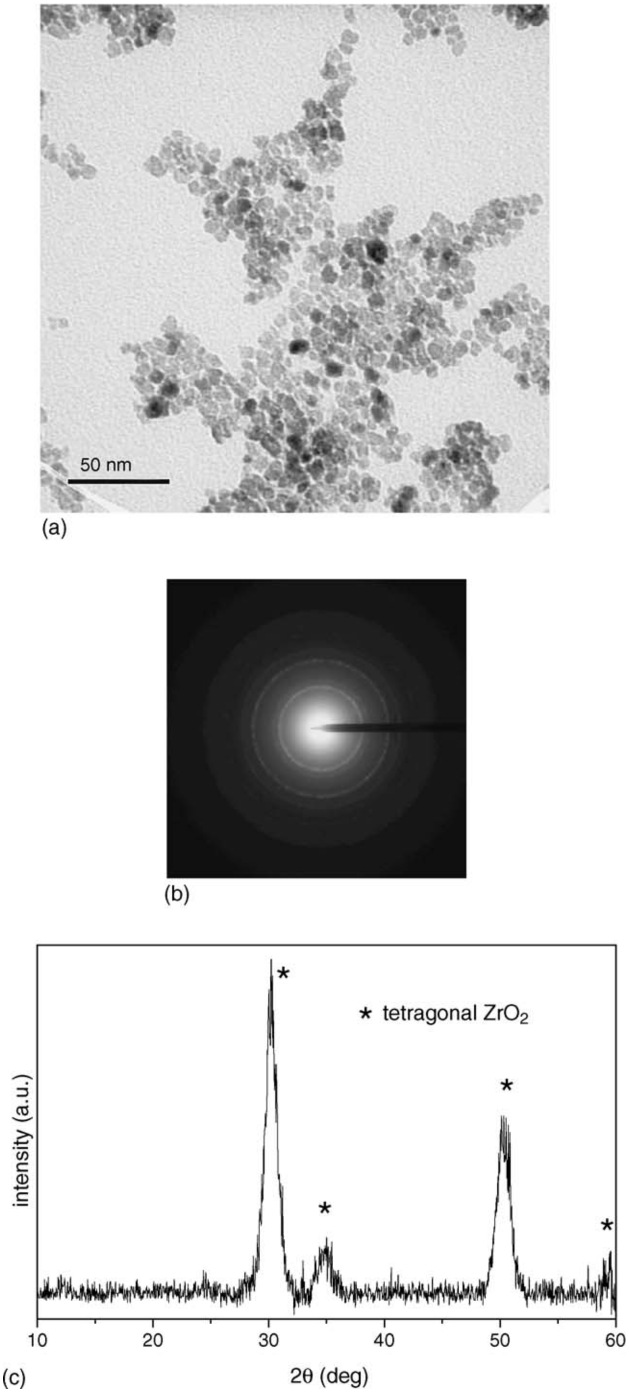

Fig. 7. TEM-image (a), electron diffraction pattern (b) and XRD-pattern (c) of hydrothermally prepared tetragonal 3Y-ZrO_2 nanoparticles.

Moreover, ζ-potential measurements of the coated YSZ cores were performed (Fig. 3b). The core–shell particles before calcination have an isoelectric point of approximately 10. This is the same as the original boehmite particles, so it can be concluded that the core is covered with a boehmite shell. After calcination, the isoelectric point of the coated powder is shifted to a lower pH (more or less pH 8), indicating that upon this treatment boehmite is converted into γ-Al_2O_3.

From PCS results, it could also be deduced that the cores were surrounded by a shell, because the mean particle diameter after the coating process was larger than before. From these PCS data, it was calculated that the mean layer thickness of the γ-Al_2O_3 shell was approximately 30 nm.

3.4. Coating of alumina cores with hydrothermal 3Y-ZrO_2

From Fig. 6a, showing the ζ-potential curves of the alumina core and hydrothermal 3Y-ZrO_2, it can be inferred that the most suitable pH value for heterocoagulation is almost 8.

PCS measurements recorded that the uncoated alumina core has a mean diameter of 180 nm at pH 8, i.e. the pH value at which the coating process will be carried out. The hydrothermally prepared 3Y-ZrO_2 particles have a primary particle size of 15–20 nm, as seen in TEM (Fig. 7a). These nanoparticles consist completely of the tetragonal phase, as can be concluded from the electron diffraction pattern (Fig. 7b) and from XRD results (Fig. 7c). At pH 8, the hydrothermally prepared 3Y-ZrO_2 particles are agglomerated, as a consequence of the low ζ-potential in this area. Their particle size, measured with PCS, is rather big – almost 340 nm – as expected.

The optimal quantity of 3Y-ZrO_2 in the shell was established to be four times (in molar ratio) the amount of alumina. Fig. 8, a TEM photograph, shows that the 3Y-ZrO_2 nanoparticles are attracted to the surface of the alumina core. Also from a ζ-potential curve of the coated and calcined powder it could be concluded that the alumina core was enwrapped by 3Y-ZrO_2. The isoelectric point was shifted to pH 5.6, which is near the isoelectric point of 3Y-ZrO_2.

After coating and calcining the alumina cores, the particle size was measured by means of PCS as well. Their was an obvious enlargement of the mean particle diameter in comparison with the core diameter before coating, indicating that the coating

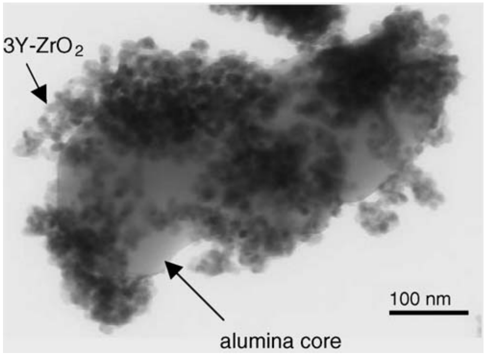

Fig. 8. TEM-photo of an alumina core coated with hydrothermally prepared 3Y-ZrO_2, calcined at 700 °C for 1 h. The rest of the sample has a similar view.

process has succeeded. From this, a layer thickness of approximately 80 nm was derived. So, during the coating itself, the shell particles will also bond to the cores and not only to similar shell material. That is why it is possible to deposit such a thin layer on the core even though the shell particles are highly agglomerated at the same pH.

4. Conclusion

By means of a heterocoagulation method, ZrO_2 and Al_2O_3 particles can be coated by a nanolayer of Al_2O_3 or ZrO_2, respectively. The shell material is quite well distributed around the cores, as confirmed by TEM-images.

It can be concluded that the heterocoagulation process is a convenient method for coating an oxide nucleus with a nanolayer of another oxide material. After all, the production of oxide–oxide core–shell particles, in particular alumina–zirconia and zirconia–alumina, is a rather new topic in literature and that is why it is promising that this coating is possible with heterocoagulation, which is a reasonably simple technique.

It is noticed that, when the coating process is carried out with boehmite particles, a more homogeneous and uniform layer around the YSZ cores is obtained, compared to coating with γ-Al_2O_3. This is probably owing to the fact that the boehmite particles are better dispersed and have a rather high ζ-potential at the circumstances, at which the coating is done. After all, the pH region in which the heterocoagulation can take place for boehmite is much larger than for γ-Al_2O_3.

Above all things, the stability of the coated and calcined powders is quite satisfactory; only very strong mechanical forces, like the one produced by a ball mill, can destroy the coatings.

From the obtained results, it can be deduced that it is possible to deposit a nanolayer of Al_2O_3 or ZrO_2 on ZrO_2 or Al_2O_3 cores, respectively, in spite of the bad quality of the dispersion at the circumstances just before coating. Getting rather bad dispersions is inherent to the heterocoagulation method, because the coating has to be done in the neighbourhood of the isoelectric points of the starting powders.

Acknowledgments

The project is supported by “het Vlaamse gewest-IWT”. M. K. Van Bael and G. Vanhoyland are post-doctoral fellows of the Fund for Scientific Research Flanders, Belgium (FWO Vlaanderen). The authors would like to thank the Materials Department of VITO for the use of the ζ-potential analyser.

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