

# Bonding of Porous Alumina Structures with Zirconia Nanoparticles

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#### Abstract

Porous alumina coatings with a final thickness in the order of 0.1 mm were produced by spraying ethanolic dispersions of particle mixtures onto steel substrates, followed by drying and heating at 500°C for 60 min. The coatings consisting only of a mixture of coarse and sub-µm sized alumina particles are generally poor in adherence and in abrasion resistance. By including a colloid of nanoscaled zirconia (d ~7 nm, calculated from the specific surface area) to the dispersion, coatings with clearly improved mechanical properties can be obtained. The zirconia fraction of 8 vol.% (related to the ceramic content) causes strong bonding between the alumina particles and the substrate.

This bonding effect is quantified by bending tests, which have been performed after spray drying the dispersions, pressing the powders to form mechanical testing beams and applying a heat treatment at 500°C. The bending tests reveal that strengths are improved at least by a factor of 5 when the nanoparticles are present in the mixture.

The described method to establish ceramic bonds in ceramic structures at temperatures, which are far below usual sintering temperatures, is a typical effect which arises in the nano size range, as the nanoparticles' high reactivity based on their large specific surface area is deployed.

Keywords: Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, Nanoparticles, Bonding, Colloidal processing, Particulate structure

#### SPAJANIE POROWATYCH STRUKTUR TLENKU GLINU ZA POMOCĄ NANOCZĄSTEK DWUTLENKU CYRKONU

Porowate powłoki z tlenku glinu o końcowej grubości rzędu 0.1 mm wytworzono rozpylając zawiesiny etanolowe mieszanin proszków na stalowe podłoża, poddane następnie suszeniu i wygrzewaniu w 500°C przez 60 min. Powłoki składające się jedynie z mieszaniny gruboziarnistych i submikronowych cząstek tlenku glinu mają generalnie słabą przyczepność i odporność na ścieranie. Poprzez wprowadzenie do zawiesiny koloidu nanometrycznego dwutlenku cyrkonu (d ~7 nm, obliczone z powierzchni właściwej) można uzyskać powłoki o wyraźnie polepszonych właściwościach mechanicznych. Udział dwutlenku cyrkonu wynoszący 8 % obj. (w stosunku do zawartości części ceramicznej) powoduje mocne połączenie pomiędzy cząstkami tlenku glinu i podłożem.

Efekt wzmocnienia połączenia znajduje ilościowy wymiar w badaniach zginania, które przeprowadzono po wysuszeniu rozpyłowym zawiesin, prasowaniu otrzymanych proszków w postać belek do badań mechanicznych i zastosowaniu obróbki cieplnej w 500°C. Badania zginania ujawniają, że wytrzymałość poprawia się przynajmniej pięciokrotnie wtedy, gdy w zawiesinie występują nanocząstki.

Opisana metoda wytworzenia ceramicznego połączenia w strukturach ceramicznych w temperaturach, które mieszczą się daleko poniżej zazwyczaj stosowanych temperatur spiekania prowadzi do typowego efektu, który powstaje w zakresie rozmiaru nano, ponieważ wprowadzana jest wysoka reaktywność nanocząstek związana z ich dużą powierzchnią właściwą.

Słowa kluczowe: Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, nanocząstka, spajanie, przetwarzania koloidalne, struktura drobnocząstkowa

# 1. Introduction

We presented previously a method of ceramic coating fabrication on the basis of zirconia by spraying a suspension on a substrate, followed by drying and a thermal treatment at intermediate temperatures around 500°C [1]. Resulting from this process, porous ceramic coatings with a certain mechanical strength and with thicknesses in the order of 0.1 mm can be obtained on rigid substrates, *e.g.*, on steel. The presented route is the way to get for example, cheap thermally [1] and electrically insulating coatings on metal parts, which could have complex shapes to mention a further advantage of the route.

To achieve a mechanical integrity and strength as well as a good adherence of the coating to the substrate, two issues have to be addressed. The first one is the bonding of the porous particle structure inside the coating and to the surface of the substrate. As shown before [1] this can be realised by using the bonding capability of small nanoparticles at temperatures far below usual sintering temperatures (*e.g.*, 500°C). This effect can be ascribed to the first sintering effects and/or to the condensation of surface hydroxyl groups [2]. The minimisation of drying and sintering shrinkage is the second important issue as this would cause the delamination of the coating from the substrate or cracking of the coating. Here, a limited bonding temperature and mixtures of particles of different size are the key. Firstly, the multimodal size distribution leads to a high packing density of particles. Secondly, a dominant fraction of large particles brings in a very low sintering activity, is able to minimise drying stress [3], and acts as "structural backbone". Wang *et al.* [4] avoided overall shrinkage during firing of a 0.2-0.6 mm coating on a rigid substrate even up to 1200°C with the so-called 'bricks and mortar' concept using 10-60  $\mu$ m ZrO<sub>2</sub> particles as a large fraction and 14 nm ZrO<sub>2</sub> nanoparticles as 'mortar'.

The zirconia nanoparticles are understood as the "mortar" in the paper of Wang *et al.* [4] and thus, a bonding function is ascribed to the nanoparticles. But, as a temperature of 1200°C is applied, intense sintering of the nanoparticles is the underlying mechanism of mechanical consolidation. Another example of bonding with nanoparticles at high temperatures (1600°C in an axial hot press) is described by Hellmig *et al.* [5]. There, the ceramic parts to be joined and the nanoparticles are made of alumina. These are the examples in the high temperature range, but in our literature research no further paper was found (next to [1, 2]) describing the bonding capability of small ceramic nanoparticles at relatively low temperatures like 500°C based on the mechanisms described in [2].

The present paper aims to clarify if the zirconia nanoparticles also bond alumina particles and if the shrinkage minimising structural backbone works when relatively small particles (~5  $\mu$ m) are used for the fraction of large particles. An important goal is to use a straightforward method to quantify the bonding effect of the nanoparticles in the particulate structure. This is realised by determining bending strengths which is a more defined method with respect to mechanical properties than measuring coating abrasion resistances only.

### 2. Experimental

#### 2.1. Ceramic raw materials

AA-5 (Sumitomo Chemical Company, Japan), corundum with a nominal particle size of 5 µm was used as a coarse fraction. The corundum AKP 50 (also from Sumitomo) with a specific surface area (*S*) of 11 m<sup>2</sup>/g (own measurement, resulting in a calculative average particle diameter of ~140 nm ( $d = 6000 \cdot S^{-1} \times \rho^{-1}$ )) was used as a particle fraction with an intermediate size.

Zirconia nanoparticles (n-ZrO<sub>2</sub>, doped with 4 mol.% Y<sub>2</sub>O<sub>3</sub>) were produced by a precipitation and hydrothermal treatment in our labs. Afterwards, as continuation of the preparation process [6], the particles were chemo-mechanically surface modified with 3,6,9-trioxadecanoic acid (TODA, Clariant, Germany) to obtain a colloid ( $d_{50}^{vol}$  = 42 nm, measured by dynamic light scattering) in ethanol. A specific surface area of 151 m<sup>2</sup>/g was measured. From this value an average particle diameter of ~7 nm can be calculated.

#### 2.2. Sample preparation

#### 2.2.1. Coatings

Two ethanolic suspensions for the spray application were prepared. The fully composed suspension contained 79.2 wt% ceramic particles (65.9 vol.% of AA-5, 26.3 vol.% of AKP 50, 7.9 vol.% of n-ZrO<sub>2</sub>). Ethanol and corundum particles

were given to the zirconia colloid to reach the mentioned solid content while mixing with a magnetic stir bar. For comparison the second suspension was composed without zirconia nanoparticles at a solid content of 78.2 wt% (71.5 vol.% of AA-5, 28.5 vol.% of AKP 50). In both cases additional TODA has been used to realise pH  $\approx$  4. For homogenisation of the mixture and deagglomeration of the corundum particles the suspensions were treated for 45 minutes with Al<sub>2</sub>O<sub>3</sub> milling spheres ( $\emptyset \approx 2$  mm) in a Turbula mixer (W. A. Bachofen, Switzerland) and ultrasonicated afterwards. Then the suspensions were sprayed on steel (material no 1.4301) substrates (100×100 mm<sup>2</sup>) with the spray applicator Minijet (Sata, Germany). After drying at 100°C the coatings have been consolidated at 500°C for 1 h.

#### 2.2.2. Beams for mechanical testing

Additional suspensions were prepared according to the previous section. They had nearly the same composition with respect to solid content and particle mixture, but here 4 wt% (related to the particle amount) of PVB (polyvinyl butyral, Mowital B 30 T, Kuraray Specialities Europe, Germany) was added as an organic binder to improve pressing behaviour and green strength. These suspensions were spray dried at 180°C in the Mini Spray Dryer B-191 (Büchi Labortechnik, Switzerland). For each beam ~1.55 g of the respective powder was axially pressed in a steel die (4×45 mm<sup>2</sup>) at 50 kN resulting in beam heights around 2.7 mm. Then, the beams underwent a thermal consolidation at 500°C for 1 h. Afterwards, they were used in mechanical testing without any machining or surface treatment.

#### 2.3. Mechanical testing and characterisation

The strength of the coating and its adherence to the steel substrate were characterised by abrasive strength testing with the Taber Abraser 5130 (Taber Industries, USA) using an abrasive roll of the CS-10F type and applying 100 load cycles. The coating thickness was measured after drying using the eddy current method with a Fischerscope MMS (Helmut Fischer, Germany).

3- and 4-point bending tests were performed on a Zwick 1446 mechanical testing machine (Zwick, Germany) with 40 mm, respectively 40 / 20 mm bearings and a cross head speed of 0.1 mm/s.

Fracture surfaces of the beams were examined by scanning electron microscopy using a Quanta 400 ESEM FEG (FEI Europe, The Netherlands) in the low vacuum mode. Abraded particles from the beams (after thermal consolidation) were examined by transmission electron microscopy using a CM 200 FEG (Philips, The Netherlands) at 200 kV.

The sintering shrinkage of axially pressed compacts ( $\emptyset$  = 5 mm, h ≈ 4 mm, ~8.5 kN) was measured in a Dilatometer L75 (Linseis, Germany).

# 3. Results and discussion

#### 3.1. Coatings

By spraying the dispersion on a steel substrate, drying and heat treating at 500°C, adhering coatings with the thick-

ness as given in Table 1 were achieved. After 100 cycles of abrasive testing a material amount was worn from the coatings, as indicated in Table 1.

Coating	Thickness [µm]	Wear [g]
without nanoparticles	62	0.446
with nanoparticles	72	0.028

Table 1. Thickness and wear of coatings.

In the case of the coating without nanoparticles, the whole coating material has been worn in the track of the abrasive roll (Fig. 1) after 80 load cycles. The different thicknesses result from the spraying process which is conducted by hand and thus does not lead to exactly the same thickness. Thicker coatings (149 / 182  $\mu$ m) were also sprayed, but they delaminated for both types (with / without nanoparticles) during thermal consolidation.



Fig. 1.  $AI_2O_3$  coatings after abrasive testing.

The different wear behaviour gives the first evidence for the observation that  $ZrO_2$  nanoparticles also bond and interconnect alumina particles during the process. But in [1], for the pure zirconia particle mixture, lower wear amounts (0.107 / 0.012 g) occurred after 100 load cycles and thicker coatings were accessible. The following reasons can be considered for the weaker mechanical properties of the actual coatings:

- The coefficient of thermal expansion of corundum  $(\alpha_{20...1000^{\circ}C} = 8.4 \cdot 10^{-6} \text{ K}^{-1} [7])$  differs stronger from the one of the steel substrate ( $\alpha \approx 16 \times 10^{-6} \text{ K}^{-1}$ ) than zirconia ( $\alpha \approx 11 \cdot 10^{-6} \text{ K}^{-1}$ , for TZP), resulting in a higher mechanical stress in the coating during the heat treatment.
- The larger tendency of the alumina coatings to shrink due to the use of smaller particles for the fraction of large particles (here: 5 µm, in [1, 4]: several 10 µm) also results in stress because of the rigid substrate.

As the coefficients of thermal expansion show, the first point is an actual detrimental mechanism for the alumina coatings. That also applies for the second point, as the dilatometric curves in Fig. 2 demonstrate.

The dilatometric curves show the first shrinkage effect up to 100°C due to water or solvent evaporation and the second one above 200°C due to binder burn out, followed by thermal expansion which is not influenced by further shrinkage up to ~1100°C. The shrinkage values shown in Table 2 can be given for the relevant temperature after subtracting the thermal expansion part from the overall length changes.



Fig. 2. Dilatometric response of pressed compacts of the particle mixtures.

Table 2. Shrinkage of pressed compacts of the particle mixtures up to 500°C.

Sample	Shrinkage [%]	
without nanoparticles	-0.3	
with nanoparticles	-1.2	

The higher shrinkage of the batch with nanoparticles can be explained with their higher specific surface area, which offers a larger adsorptive space for water or solvent and binder. The resulting higher amounts of dried- or burned-out matter lead to higher shrinkages. Previously, in the zirconia system a shrinkage of -0.09 % was observed at 500°C for the sample with nanoparticles [2]. The lower shrinkage value for the particle mixture used there confirms that a structural backbone made of relatively larger particles has a better capability to prevent shrinkage.

As the quantitative bonding capability of the nano-particles is in the focus of the present work, we did not follow approaches for the optimisation of the coatings, such as the use of larger particles for the large particle fraction or the use of intermediate coatings for the compensation of the thermal expansion difference.

## 3.2. Beams in the mechanical test

Our approach to characterise the mechanical strength of nanoparticle bonded structures is a common bending test. During thermal consolidation of the bending beams, stress generating mechanisms resulting from length changes relative to the substrate do not apply.

17 beams were pressed of each particle mixture. The densities shown in Table 3 were calculated from the beam weight and dimensions after the treatment at 500°C.

As a small shrinkage is taking place, it can be concluded that a high pressing density is achieved, which can be ascribed to an effective packing of the particle mixture.

Table 3. Density of beams after the	treatment at 500°C.
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Beams	Density [g/cm <sup>3</sup> ]	Relative density [%TD <sup>*</sup> ]
without nanoparticles	$2.8\pm0.06$	70
with nanoparticles	$2.9\pm0.05$	71

\* % of theoretical density

The strength of the beams was measured in the 4-pointbending test (Table. 4).

Table 4. Apparent strength in the 4-point-bending test.

Beams	Strength [N/mm <sup>2</sup> ]	Pieces
without nanoparticles	$1.0\pm0.4$	10
with nanoparticles	$\textbf{6.8} \pm \textbf{0.6}$	10

It was observed that nearly all beams cracked at the position of one of the upper bearing rolls. So it was concluded that the occurring small forces (< 10 N) were too small to tilt the upper bearings in order to achieve equal force transmission from both upper rolls to the beam. Therefore the given fracture stresses are considered to be smaller than the values that could have been achieved in the case of symmetrical load, and therefore additional 3-point-bending tests were made (Table 5). The strength levels resulting from 3-point-bending are much higher than usually in comparison to the 4-point bending test (usually slightly lower values are achieved in 4-point-bending due to the larger tested volume at the maximum load stress), confirming the assumption that an unequal load leads to apparent lower strengths.

Table 5. S	Strength	in	the	3-point-	bending	test.
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Beams	Strength [N/mm <sup>2</sup> ]	Pieces
without nanoparticles	$2.8\pm0.3$	7
with nanoparticles	14.1 ± 1.4	6*

\* one piece damaged when demoulded from the pressing die

So, the 3-point-bending strengths can be considered as correct data. Nevertheless, the 4-point bending "unsymmetrical load values" are given as they also enable the comparison of samples with and without nanoparticles. Both mechanical measurement series confirm clearly the bonding effect of the nanoparticles as, by their use, the strength level is increased by a factor of ~7 or ~5, respectively.

The achieved strength levels are certainly much smaller than for densely sintered alumina (a typical value is 400 N/mm<sup>2</sup> [8]). But, they are reasonable and competitive with respect to the applied temperature and the resulting porous microstructure. For comparison with a lower limit, a flexural strength of 0.5 N/mm<sup>2</sup> can be given for a green body, which was obtained by isostatic pressing (200 MPa) of 0.6 µm alumina particles with 3 wt% polyacrylic acid binder [9]. Hardy and Green [10] report a biaxial flexure strength of around 15 N/mm<sup>2</sup> for porous specimens made of 0.38 µm alumina particles after a heat treatment at 800°C. Using the

nanoparticles, a similar strength level (3-point-bending) was already achieved in the present work at 500°C.

## 3.3. Microstructure

Fig. 3 shows the fracture surface of a bending beam. Here and at higher magnifications no flaws could be recognised, allowing the conclusion that the spray dried granules had good pressing properties. A typical distribution of the  $\mu$ m sized alumina particles on the large ones can be seen in Fig. 4.



Fig. 3. SEM picture of the fracture surface of a bending beam.



Fig. 4. SEM picture showing coarse and sub-µm alumina particles.

On the SEM picture in Fig. 5 and on the TEM pictures in Figs. 6 and 7, the zirconia nanoparticles can be seen. A few single nanoparticles or small agglomerates can be observed on the alumina particle surfaces, but the nanoparticles mainly appear in agglomerates with their size being in line with the measured average agglomerate size in the used colloid  $(d_{50}^{vol} = 42 \text{ nm})$ . So as it could be expected, these agglomerates were not deagglomerated during the mild milling of the entire particle mixture as this step was used to deag-



Fig. 5. SEM picture showing zirconia nanoparticles and sub-µm alumina particles.



Fig. 6. TEM picture showing zirconia nanoparticles and sub- $\!\mu m$  alumina particles.

glomerate the alumina particle types and to homogenise all particles. The homogenisation of the zirconia nano-particles was incomplete as also alumina particles not being in contact with zirconia can be observed in Fig. 6.

In the TEM pictures (Figs. 6 and 7) zirconia nano-particles can be found directly between alumina particles as well as in the neighbouring space next to alumina contact areas, where zirconia particles or agglomerates are in contact to both alumina particles. In these positions the bonding and connecting effect is plausible. Also alumina particle contacts without involved zirconia nano-particle can be found due to limited homogenisation (Fig. 6).

# 4. Conclusions

The feasibility of bonding porous particulate structures with zirconia nanoparticles is demonstrated for a mixed



Fig. 7. TEM picture showing zirconia nanoparticles and sub-µm alumina particles.

phase system, here on the basis of alumina particles to be bonded. For the first time, the bonding capability of small (d =  $\sim$ 7 nm) zirconia nanoparticles at 500°C has been quantified on the basis of a mechanical bending test. Nanoparticles used as bonding elements achieve an increase of 3-point-bending strength by a factor of ~5, which gives a clear evidence of the effect.

In comparison to our previous work [1, 2], smaller alumina particles were used as a structural backbone (dominant fraction of large particles), resulting in a slightly higher shrinkage of the structures at the consolidation temperature of 500°C. In shrinkage tolerant freestanding parts like the beams, this does not cause problems but for coatings on rigid substrates it appears advantageous to use larger particles with respect to shrinkage minimisation.

As bonding occurred between different particles in the presented system, the behaviour of a lot of other possible phase combinations, especially based on other nanoparticles, could be an interesting topic for future examinations.

In the case of the used zirconia nanoparticles better deagglomeration states can be achieved [6, 11]. So, it is another interesting question for future work if the mechanical integrity of the particulate structure could be improved with a more homogeneous distribution of less agglomerated bonding nanoparticles.

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