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The effect of nanometric zirconia particle additives on microstructure and mechanical properties of dense alumina

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Abstract

Zirconia additives have favourable influence on mechanical properties of dense alumina polycrystals. It results from the martensitic transformation of tetragonal zirconia particles into monoclinic symmetry at the crack tip propagating through a material. Usually applied zirconia particles were of sub-micrometer or micrometer sizes. In the present work nanometric zirconia particles prepared by hydrothermal crystallization technique were introduced into the alumina matrix. Both, zirconia and alumina powders were homogenized in an aqueous suspension of pH selected on the basis of the zeta (ξ) potential measurements. It was found that this factor influences greatly strength of the resulting powder agglomerates and hence mechanical properties of the sintered material.

***Keywords**: Alumina - zirconia, ceramic composites*

I. Introduction

The favourable influence of zirconia additives on mechanical properties of dense alumina polycrystals is known since late seventies [1]. It is due to the martensitic transformation of zirconia particles of tetragonal symmetry to their monoclinic form at the crack tip. This transformation consumes energy of elastic strain which otherwise would be the driving force for the propagation of the crack through the material. This is the main factor responsible for the increase of the fracture toughness over the value observed in case of the pure alumina. An essential increase of the ware resistance of such material has been also observed.

So far sub-micrometer or even micrometer zirconia particles have been used. In the present study, zirconia powder with crystallite sizes of about 10 nm and alumina with grain sizes of about 175 nm were applied. Uniform microstructure of such particulate composites influences essentially their properties. That is why we have focused in our study on the homogenization conditions of both powders, i.e. nanometric zirconia and sub-micrometric alumina particles. Homogenization itself was performed in the aqueous suspension with carefully controlled pH value.

II. Experimental

The starting solution of $ZrOCl_2$ with 1.7 M concentration was introduced to the vigorously stirred aqueous solution of ammonia. The final pH=9 lead to quantitative precipitation of the zirconia gel. The resulting gel was carefully washed with distilled water in order to remove NH_4Cl and subjected to hydrothermal treatment at 240°C for 4h under the autogenous water vapour pressure. It lead to crystallization of nanometric zirconia particles. Details of the method are described elsewhere [2–6]. The powder was kept in the water suspension and its concentration was determined by drying. Alumina AKP-30 produced by Sumitomo was applied in our study.

X-ray diffraction, $CuK\alpha_1$ irradiation, (X'PertPro, Phillips PANanalitical) equipment allowed us to determine phase composition of zirconia powder. Tetragonal and monoclinic phases of ZrO_2 were found. Based on the (111) line broadening of the tetragonal phase and using Scherrer formula, crystallite size of the powder was calculated. Specific surface area was determined by BET method using apparatus Nova 1200 (Quantachrome). Zeta (ξ) potential vs. pH of the suspension was measured with Zetasizer Nano-ZS apparatus (Malvern).

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Homogenization of alumina and zirconia powders was conducted by attrition milling for 1h in an aqueous slurry with pH=3 and 9. The selected pH levels were selected on the basis of zeta potential measurements. Acidic conditions were adjusted with nitric acid introduced to the system and pH=9 with ammonia. Water with the selected pH level was prepared before introducing powders in it. Level of pH was controlled during homogenization. In each case 10 vol% zirconia additive was applied. Samples with the size 60×60×7 mm were uniaxially dry pressed under 50 MPa and isostatically repressed under pressure of 250 MPa. Then the samples were sintered at 1600°C for 4h with the heating rate of 5°C/min. Bars with 50×5×3 mm size were cut with the diamond saw. They were used for three point bending strength measurements; 4 mm distance between supports was used. In the same bar-samples notch was cut in with 0.1 mm diamond saw. They were used for fracture toughness determination (K_{Ic}). For comparison, samples made of pure Al_2O_3 were also prepared. Mechanical testing was performed using Zwick-Roell machine (model 1.5). Young's modulus of the sintered samples was determined by the ultrasonic method [7].

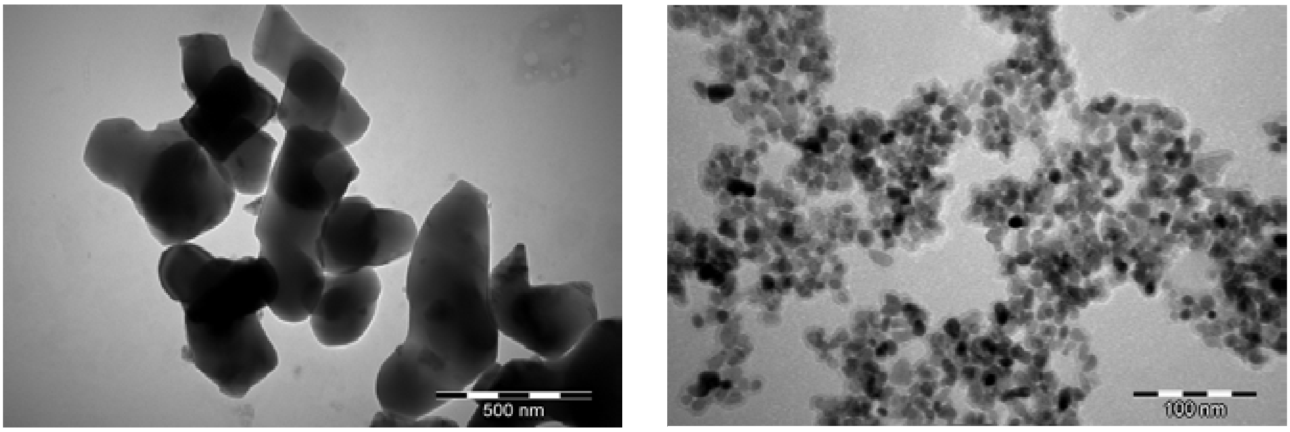
III. Results and discussion

Properties of the powders are listed in Table 1. Fig. 1 shows transmission electron micrographs of zirconia and alumina powders.

Both powders differ substantially in their particle sizes. In the case of zirconia powder D_{BET} and D_{111} practically are equal to each other. It suggests isometric shape of the particles which is corroborated by the TEM micrograph (Fig. 1). What is more, the particles do not form inter-crystalline contacts. If it were so, the relation $D_{BET} > D_{111}$ should be expected.

The aim of this work was to check the effect of the homogenization conditions on the composite powder properties as well as characteristics of the resulting materials. Fig. 2 shows zeta (ξ) potential vs. pH of the suspension. These plots allow us to distinguish two ranges of pH. Under acidic conditions all particles have charge of the same sign, i.e. they repel each other. At pH=9 zirconia particles' charge is of opposite sign than the alumina grains and alumina and zirconia particles should attract each other. This situation causes so called heterofloculation effect and should improve homogenization of the system [8].

It was found that deflocculated suspension (pH=3) after drying forms succinct, hard body difficult to grind in a mortar. Most probably repelling forces between particles facilitate their dense packing. In case of flocculated suspension (pH=9) repelling forces between the same particles are much weaker due to the essentially lower values of their zeta potentials. Such suspension after drying forms much less succinct powder; it is soft and can be easily ground in a mortar. These macroscopic observations are corroborated by the pore size



a) b)

Figure 1. Transmission electron micrograph of alumina (a) and zirconia (b) powders

Table 1. Properties of the powders

Powder	Phase composition	S_w [m^2/g]	D_{BET} [nm]	D_{111} [nm]
ZrO_2	*t* – 71.8 wt.% *m* – 28.2 wt.%	97.6	10.1	10.0
Al_2O_3	α-Al_2O_3	8.6	174.9	-

t - tetragonal zirconia, m - monoclinic zirconia, S_w - specific surface area, D_{BET} - particle size determined on the basis of the specific surface area, D_{111} - crystallite size determined on the basis of X-ray line (111) broadening of the tetragonal phase

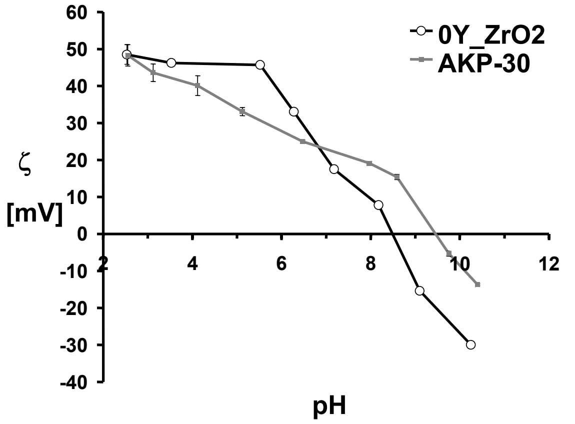


Figure 2. Zeta potential vs. pH of the alumina and zirconia suspensions

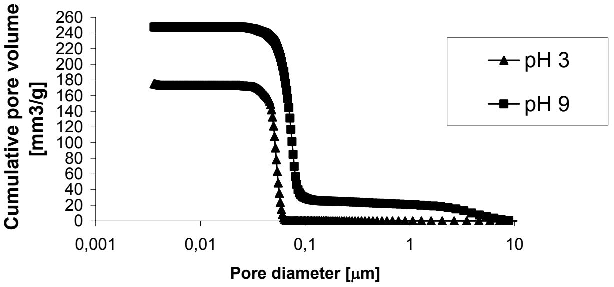


Figure 3. Cumulative pore size distribution curves in dry sediments of alumina-powders homogenized in suspensions with indicated pH values

distribution measurements in dried sediments of both powders (Fig. 3). It can be noticed that pores in the system homogenized under acidic conditions (pH=3) are shifted towards smaller sizes and the total porosity of such sediment is lower. Based on these measurements porosity of these sediments could be assessed. It equals 42.3% and 51.2% for the systems processed under acidic and basic conditions, respectively. Effect of the state of suspension flocculation on the succinctness of dried sediments is known in case of the single phase powders [9], but not in case of the polyphase systems.

In Table 2 densification of the sintered samples and their elastic moduli are shown. Densification of the composite, prepared under acidic conditions, is lower than that processed in the basic suspension. The same tendency occurs in the case of modulus of elasticity. Pure alumina samples reached the highest densification and modulus of elasticity. This can be explained by the negative effect of inert inclusions on densification during sintering of ceramic powders [10,11]. It is well known that elastic properties of polycrystalline materials strongly depend on their densification. The higher densification results in the higher values of the modulus of elasticity.

In Table 3, bending strength and fracture toughness of the sintered materials are shown. The highest strength occurs in the material homogenized in the alkaline suspension and the lowest in the one processed under acidic conditions. In the latter case, it suggests existence of the microstructural defects, which is also indicated by the lower densification of this material and its lower modulus of elasticity. Such defects, caused by the presence of hard agglomerates in the starting powder, are well visible in SEM micrographs (Fig. 4), both in the scale of hundreds micrometers as well as in the scale of one micrometer. They play the role of stress concentrators and by itself decrease strength of the material. However, fracture of this material is relatively high. It is well known that defects, which correspond to the discontinuities in the material, limit lengths of the crack way passing through the material and improve its fracture toughness. Quite different microstructure shows the material derived from the powder homogenized in suspension with pH=9 (Fig. 5). Zirconia inclusions (bright spots) are evenly distributed and situated mainly in the grain boundaries. This material reveals the highest fracture toughness and strength (Table 3).

Table 2. Densification and Young's modulus of the sintered samples

Material	Apparent density [g/cm^3]	Relative density [% TD]**	Young's modulus [GPa]
Al_2O_3	3.952 ± 0.004*	99.05 ± 0.10	372 ± 23
Al_2O_3+10 vol% ZrO_2, pH=3	3.969 ± 0.006	94.52 ± 0.14	323 ± 8
Al_2O_3+10 vol% ZrO_2, pH=9	4.001 ± 0.002	95.28 ± 0.05	354 ± 4

* Confidence interval at 95% confidence level
** % theoretical density

Table 3. Bending strength (σ) and fracture toughness (K_{Ic})

Material	σ [MPa]	K_{Ic} [MPa·m$^{1/2}$]
Al_2O_3	380 ± 15*	4.01 ± 0.10
Al_2O_3+10 vol% ZrO_2, pH=3	235 ± 18	4.70 ± 0.14
Al_2O_3+10 vol% ZrO_2, pH=9	415 ± 13	4.77 ± 0.09

* Confidence interval at 95% confidence level

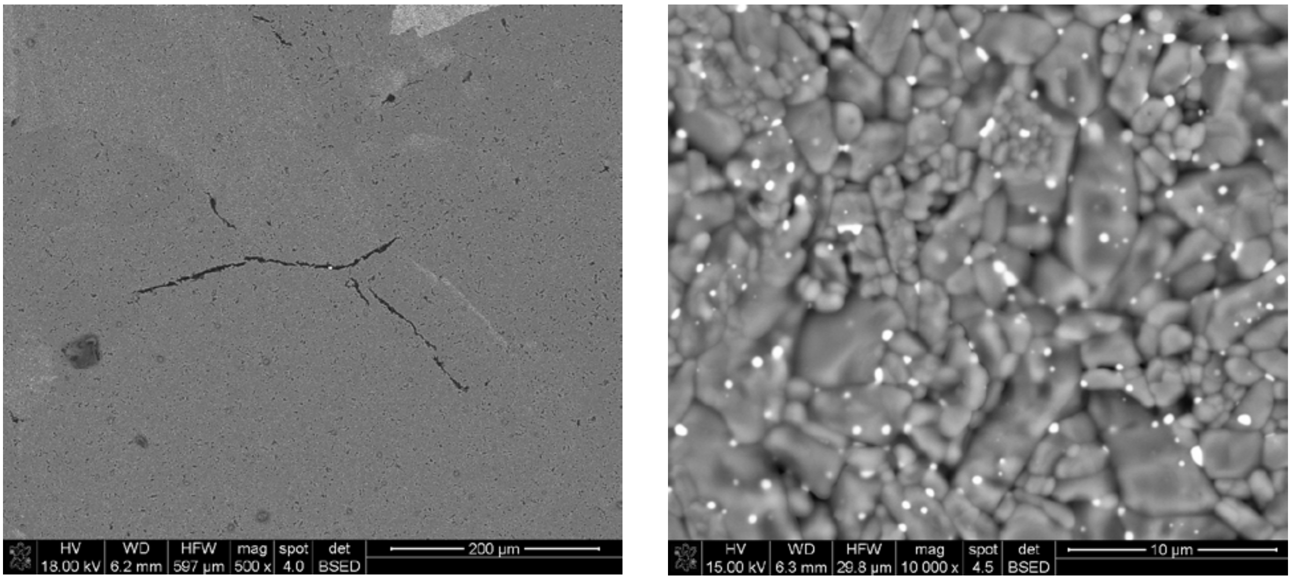


Figure 4. Microstructure of the material homogenized in the suspension with pH=3

The size of zirconia inclusions are of an order of magnitude higher than the crystallite size of the starting zirconia particle. The reason for this fact is not quite clear. Such behaviour was observed in zirconia polycrystal derived from the well deflocculated zirconia nanometric powder [12]. In case of alumina-zirconia composite it cannot be excluded that zirconia particles are dragged with alumina-zirconia boundaries. It was shown [13] that it leads to the coagulation of zirconia particles.

IV. Conclusions

Conditions of homogenization of alumina and nanometric zirconia particles have essential influence on the properties of the resulting powders. The dispersed system mixed in the acidic suspension (pH=3) is composed of hard agglomerates. Microstructure of the sintered material derived from such powder shows defects in the scale of one to hundreds micrometers and, hence it causes low strength of the material. Microstructure of the material derived from the powders homogenized under alkaline conditions (pH=9) has no such defects. It results in the material of the highest strength and fracture toughness. Size of the zirconia inclusions is about one order of magnitude higher than the crystallite size of the hydrothermally crystallized zirconia particles. Reason for this phenomenon is not quite clear.

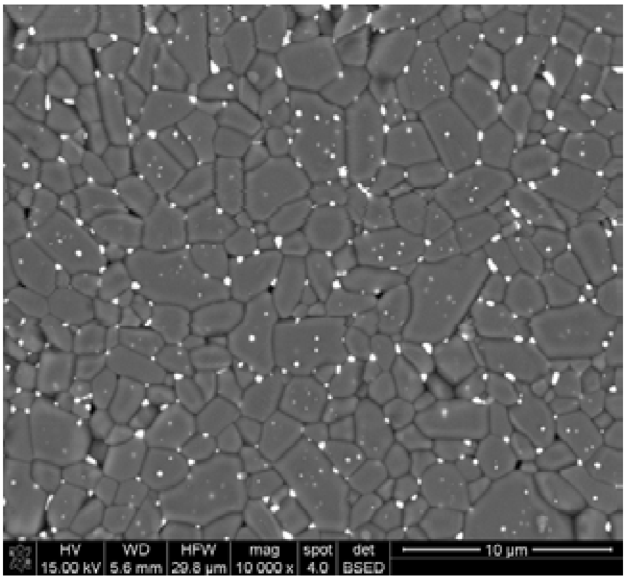


Figure 5. Microstructure of the material homogenized in the suspension with pH=9

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