Influence of elongated zirconia particles on microstructure and mechanical properties of yttria stabilized zirconia polycrystals

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Abstract

Yttria stabilized tetragonal zirconia polycrystals were prepared using mixtures of two different powders. One is composed of nanometric particles of 3.5 mol% Y_2O_3 solid solution in ZrO_2 and the other one of pure zirconia particles. The latter shows elongated particles of about 200 nm length and monoclinic symmetry and the former consists of isometric tetragonal particles of about 7 nm size. Both powders were synthesized under hydrothermal conditions at 240 °C in water (the 3.5 mol% $Y_2O_3 - ZrO_2$ solid solution) or in 4 M NaOH solution (the pure ZrO_2 powder). Two homogenous mixtures of these powders were prepared; the one with 5 wt.% and the other one with 10 wt.% of the elongated zirconia particles. Compacts of 10 mm diameter were isostatically pressed (250 MPa) and sintered in a dilatometer furnace at 1400 °C with no soaking time. A set of samples heated up to the selected temperatures allowed us to follow phase changes of the materials vs. temperature by X-ray diffraction. It was confirmed that all materials show tetragonal symmetry at the final temperature (1400 °C). Density and mean grain size decrease with the elongated zirconia particle additives. The dense samples were polished and their hardness and fracture toughness were determined by Vickers indentation. No hardness changes, due to the elongated zirconia particles additives, were observed, but essential increase of fracture toughness occurred. The observations of the crack runs suggest crack deflection as a potential mechanism of the fracture toughness increase.

Keywords: zirconia, hydrothermal crystallization, composites

I. Introduction

Zirconia shows three polymorphs: i) the low temperature one of monoclinic symmetry, ii) the tetragonal modification which occurs at the intermediate temperature range and iii) the cubic one - the highest temperature polymorph. The most interesting for the mechanical properties of the material is the transformation of the tetragonal to the monoclinic polymorph (t→m) at the end of the crack running through the material. It has a diffusion-less, martensitic character. The transformation of tetragonal symmetry grain to the monoclinic one at the crack tip leads to a few percent volume increase of the system. This phenomenon is responsible for the increased fracture toughness of the zirconia based materials. It is due to the consumption of the strain energy

by the t→m transformation, which otherwise would be used to propagate the crack. The key problem in utilization of this phenomenon is retention of the tetragonal symmetry grains in the dense polycrystal. There are two factors which are responsible for this effect: one of them is constituted by sufficiently small grains of the polycrystal. They should be smaller than the so called critical grain size, i.e. the size above which a spontaneous transformation of the tetragonal grains to the monoclinic form occurs during cooling of the system after sintering. The second factor is related to the presence and concentration of oxides which form solid solution with zirconia. The list of such oxides comprises of CaO, MgO, Y_2O_3, TiO_2 and other oxides of some rare elements.

Some of our studies were devoted to zirconia and the zirconia solid solution crystallization under hydrothermal conditions. They dealt with the subjecting amorphous zirconia gel or zirconia gel, doped with some ions

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to the hydrothermal treatments at 250 °C for 4 h. During this process the X-ray amorphous gel transforms into its crystalline form. The process performed in the pure water under the autogenous water vapour pressure results in nanometric (up to 10 nm) isometric particles of tetragonal or cubic symmetry, depending on the solute concentration. Yet the same temperature and time conditions, but performed in the strong hydroxides (NaOH, KOH, LiOH), led to the elongated particles of monoclinic symmetry. Their longer size is parallel to the c-axis of the monoclinic zirconia polymorph [1]. These investigations on the zirconia crystallization under hydrothermal conditions were already published in previous papers [2–6].

In the present work two mixtures of nanometric zirconia-yttria powder and pure zirconia elongated particles both crystallized under hydrothermal conditions were prepared. The latter were randomly distributed within the nanometric zirconia-yttria matrix. The microstructure and some properties of the sintered materials were investigated.

II. Experimental

Yttria stabilized tetragonal zirconia polycrystals were prepared using mixtures of two different powders (Fig. 1). The first one was zirconia-yttria (3.5 mol%) solid solution powder (denoted as 3.5YZ-0) with nanometric crystallite sizes and isotropic crystallite shape. The other one was pure zirconia powder (denoted as 0YZ), characterized by elongated crystallites.

In the case of the pure zirconia powder the zirconium oxychloride (ZrOCl$_2$) solution (2.1 M concentration) was introduced to the NaOH (4 M) solution. The precipitated gel was then subjected to the hydrothermal treatment at 240 °C for 4 h. So, the crystallization process proceeded in the NaOH + NaCl solution. Then the powder was washed with distilled water in order to remove Cl$^-$ and Na$^+$ ions from the system.

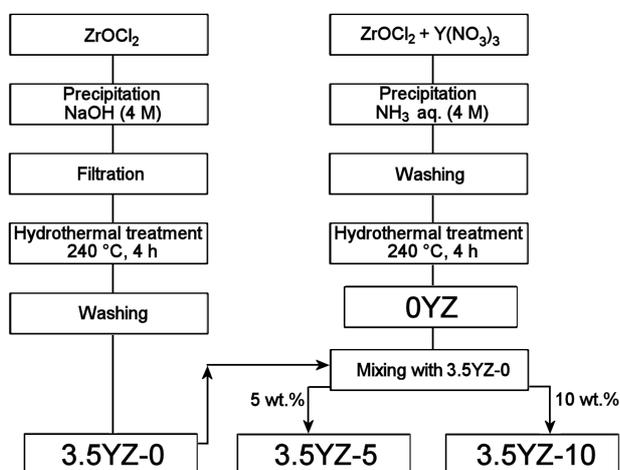In the case of the 3.5YZ-0 solid solution yttria was

introduced to the starting ZrOCl$_2$ solution as the nitrate solution prepared by dissolving Y$_2$O$_3$ in nitric acid. Ammonia aqueous solution was used as a precipitating agent. The co-precipitated gel was washed with distilled water until no reaction for Cl$^-$ ions with AgNO$_3$ occurred in the filtrate. Then it was subjected to the hydrothermal treatment at 240 °C for 4 h.

In addition, the 3.5YZ-0 powder was mixed with 5 and 10 wt.% of the synthesized pure zirconia powder (having elongated crystallites) to prepare two mixed powders 3.5YZ-5 and 3.5YZ-10, respectively (Fig. 1). The pure zirconia powder, crystallized under basic conditions, was introduced into the suspension containing 3.5YZ-0 zirconia yttria powder by vigorous ultrasonic mixing. In order to retain the mixture homogeneity, it was immediately frozen by introducing it to liquid nitrogen and freeze dried, using the SRK System Technik (mod. GT2 Basic) equipment. The prepared powders consisted of extremely soft agglomerates [7]. This helped to make uniform powder compacts after pressing. The powders were characterized by measuring their specific surface area by nitrogen adsorption (Quantochrome Instruments, NOVA 1200e) and transmission electron microscope (Tecna FEG, 200 kV). Uniaxial pressing (50 MPa), followed by cold isostatic repressing under 250 MPa, was applied to prepare cylindrical samples of 10 mm diameter and about 3 mm thickness. They were used to measure shrinkage of the samples with the temperature increase rate of 5 °C/min up to 1400 °C by Netzsch DIL 402C dilatometer. Sintering was also performed in the dilatometer furnace to the preselected temperatures again with no soaking at each temperature step. X-ray diffraction (CuKα radiation, X'Pert Pro, Panalytical) was used to determine phase composition of the powders and sintered samples.

The samples sintered at 1400 °C were polished and thermally etched at 1150 °C to reveal their microstructure. Such samples were used to determine their 3D mean grain size by the Saltykow method and the 3D grain size distribution by the Schail-Swartz-Saltykow technique.

Hardness and fracture toughness were measured on the polished but not etched samples by using the Future Tech (Japan) equipment. In the case of hardness, the load of 1 kg was applied. It did not lead to any crack formation. Higher load (3 kg) and resulting Palmqvist cracks were used to calculate the K_{Ic} values, based on the Niihara formula [8,9]:

$$K_{Ic} = 0.018HV^{0.6}E^{0.4}2al^{0.5} \qquad (1)$$

where l is the length of the crack, a is half of the indent and Young modulus of $E = 200$ GP was assumed.

III. Results and discussion

The specific surface areas of the pure zirconia powder crystallized in the alkaline solution (0YZ) and the 3.5YZ powder, hydrothermally processed in distilled
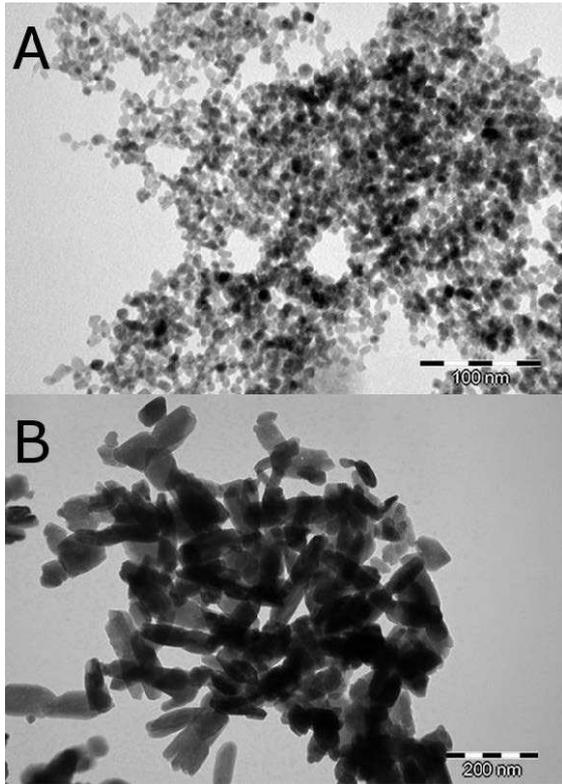

Figure 1. Preparation route of ZrO$_2$ and ZrO$_2$ + Y$_2$O$_3$ powders

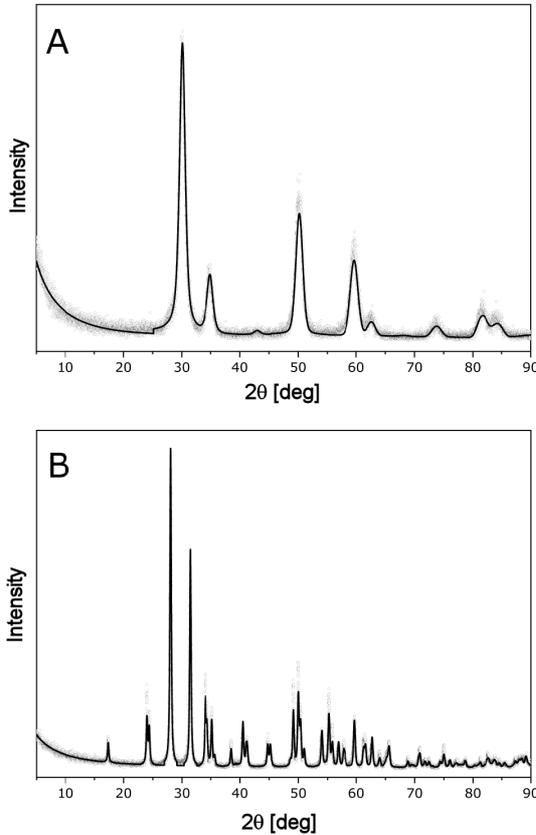**Figure 2. TEM micrographs of the synthesized powders: a) 3.5YZ-0 and b) 0YZ**

Figure 3. X-ray diffraction patterns of the synthesized powders: a) 3.5YZ-0 and b) 0YZ

water are 21.96 ± 0.03 m^2/g and 141.37 ± 0.77 m^2/g, respectively. This, together with TEM observations (Fig. 2) indicates that the latter one is much finer. The powder crystallized in the alkaline medium shows elongated crystallites and those processed in distilled water are isometric in shape and nanometric in size (Fig. 2). Both powders differ also in their phase composition. The X-ray diffraction pattern (Fig. 3) of the material crystallized in alkaline medium proves that it possesses monoclinic symmetry. The finer powder is totally tetragonal. The effect of crystallite size and composition on the crystallography is well known in zirconia systems.

The pure 3.5YZ-0 and mixtures of two powders, prepared using 5 and 10 wt.% of the elongated zirconia particles, were compacted and tested. The data presented in Table 1 indicate that addition of 5 and 10 wt.% of elongated particles do not influence the green compact density. So, shrinkage during sintering can be directly compared. Dilatometric curves (Fig. 4) clearly show that addition of the elongated particles slows down shrinkage of the systems. This is most probably due to the fact that the additive powder is essentially coarser than the matrix powder. Some part of this effect may be attributed to the elongated shape of the pure zirconia powder. Chemical homogenization of the systems during sintering should also be considered. The low temperature shrinkage is related to the desorption of water layers from the high surface of the nanometric powder [6,10].

The phase composition of the samples sintered in the dilatometric furnace up to the indicated temperatures determined by X-ray are shown in Table 2. It seems reasonable to conclude that at the highest temperature total chemical homogenization of the system occurs. It

Table 1. Density of the powder compacts

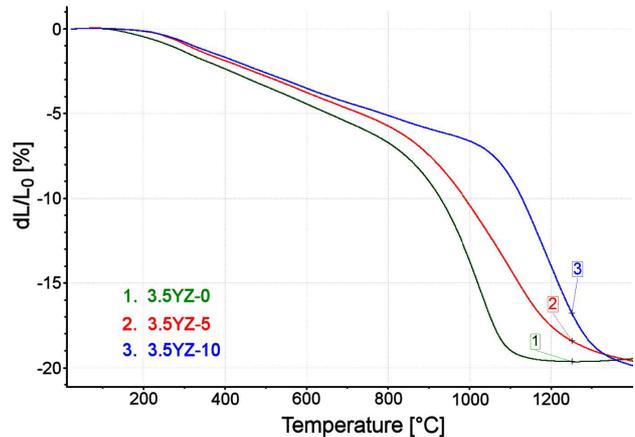| Powder	Density [g/cm^3]
3.5YZ-0	2.89 ± 0.04
3.5YZ-5	2.87 ± 0.08
3.5YZ-10	2.88 ± 0.05

Figure 4. Dilatometric curves of the powder compacts 3.5YZ-0 (1), 3.5YZ-5 (2) and 3.5YZ-10 (3)

Table 2. Phase composition of the samples heated up to different temperatures measured by X-ray diffraction (nominal composition comes from the starting mixture proportions, t - tetragonal phase, m - monoclinic phase)

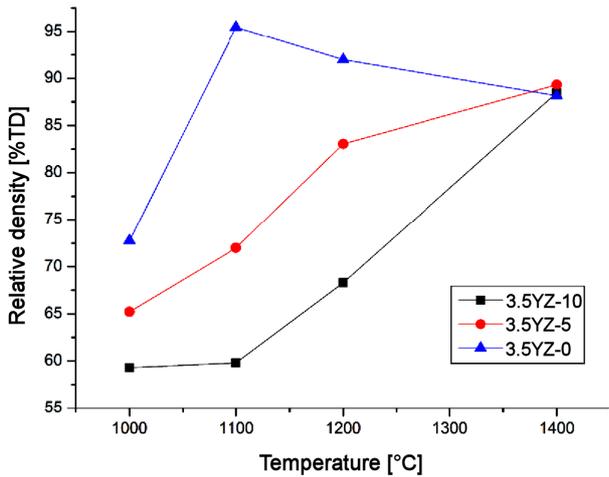| Temperature [°C]	3.5YZ-0	3.5YZ-5	3.5YZ-10
20 nominal	*100% t*	*95% t + 5% m*	*90% t + 10% m*
20	100% t	92.5% t + 7.5m	89.0% t + 11.0% m
1000	100% t	90.9% t + 9.1% m	78.2% t + 21.8% m
1100	100% t	92.7% t + 7.3% m	78.9% t + 21.1% m
1200	100% t	98.6% t + 1.4% m	90.7% t + 9.3% m
1400	100% t	100% t	100% t

Figure 5. Densities of the samples sintered in dilatometer furnace (theoretical density was assumed to be 6.0 g/cm³)
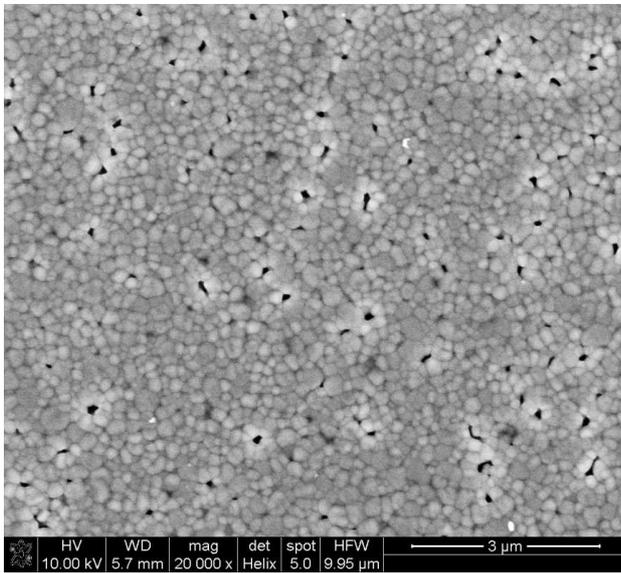

Figure 6. SEM micrograph of the sample compact 3.5YZ-0 with no coarser zirconia particles addition, sintered in dilatometer furnace

results in the fully tetragonal phase composition of the samples. The changes in their densities are shown in Fig. 5. In the case of the materials 3.5YZ-5 and 3.5YZ-10 with 5 and 10 wt.% addition of the elongated particles it increases with temperature. However, in the case of the nanometric powder compact 3.5YZ-0, with no coarser zirconia powder addition, some decrease of density is observed at temperatures surpassing 1100 °C. It should be attributed to the water vapour emission from the system containing closed pores. It leads to some expansion of the compact visible in Fig. 4, resulting in the decreased density (Fig. 5) and could be also visible in the SEM picture as a secondary porosity (Fig. 6).

The samples sintered in the dilatometer furnace at 1400 °C were polished and used to measure hardness and K_{Ic} values. The results in Table 3 show that these additives do not affect hardness but lead to the increased fracture toughness of the materials. The latter result was additionally confirmed by the crack length (CL), measured in the SEM micrographs along the crack edges, starting from the crack origin up to its end. The SEM observations show that cracks in each case run through grain boundaries, as exemplified in the case of the mate-
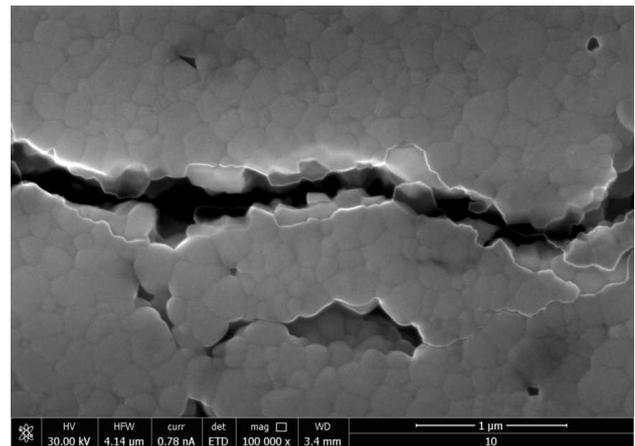

Figure 7. Crack in the material 3.5YZ-5 sintered at 1400 °C in the dilatometer furnace

Table 3. Hardness (*HV*), fracture toughness (*K_Ic*) and crack length along edges (*CL*) of the samples sintered in dilatometer furnace at 1400 °C (rate of temperature increase was 5 °C/min no soaking time)

Material	*HV* [GPa]	K_{Ic} [MPa·m$^{1/2}$]	*CL* [μm]
3.5YZ-0	10.91 ± 0.16	8.04 ± 0.13	44.9 ± 0.74
3.5YZ-5	11.04 ± 0.27	9.04 ± 0.35	38.2 ± 0.58
3.5YZ-10	11.24 ± 0.15	10.47 ± 0.25	26.2 ± 0.26

rial with 5 wt.% of elongated particles addition (Fig. 7). So, the observed fracture toughness increase should be most probably attributed to the crack deflection mechanism.

Thermal etching of the polished samples, sintered in the dilatometer, allowed us to reveal microstructure of these materials. Figure 8 is one of the examples. It is interesting to notice that no elongated particles are visible in the materials with 5 and 10 wt.% addition of such particles. Therefore, it can be postulated that elongated particles grow during sintering in the direction perpendicular to their longer axis. We can imagine this as a process of adjusting those crystallites nanometric and isometric in shape to the more flat surface of the elongated particles.

Figures 9-11 show grain size distribution of the materials sintered in the dilatometer furnace at 1400 °C. It can be seen that the smaller is the 3D mean grain size the higher is the concentration of the elongated particles. They act as the grain growth inhibitors. Simultaneously, the content of the smallest grains increases and the largest grains decrease with this addition.

IV. Conclusions

Yttria stabilized tetragonal zirconia polycrystals were prepared using mixtures of two different powders: nanometric $ZrO_2/3.5 Y_2O_3$ solid solution powder and pure zirconia powder composed of much coarser elongated particles. These additions slow down the rate of shrinkage of the system. The higher is the concentration of the additive the higher is fracture toughness of the resulting material. Most probably the crack deflection mechanism is operating in this case related to the microstructure changes. It cannot be excluded that zirconia transformation ability increases due to the decreased Y_2O_3 concentration from 3.5 to 3.14 mol% with ZrO_2 elongated particles additives.

References

1. M.M. Bućko, K. Haberko, "Mechanical anisotropy in the zirconia toughened alumina", *J. Mater. Sci.*, **34** [24] (1999) 6157–6163.
2. W. Pyda, K. Haberko, M.M. Bućko, "Hydrothermal crystallization of zirconia and zirconia solid solutions", *J. Am. Ceram. Soc.*, **74** [10] (1991) 2622–2629.
3. K. Haberko, W. Pyda, "Preparation of Ca-stabilized zirconia micro powders by hydrothermal method", pp. 774–783 in *Science and Technology of Zirconia II, Advances in Ceramics*, V. 12. Eds. N. Claussen, M. Ruhle, A.H. Heuer. The American Ceramic Society, Columbus, OH, 1984.
4. M.M. Bućko, K. Haberko, "Mechanism of the hydrothermal crystallization of zirconia", pp. 2072–2075 in *Euro Ceramics V, Key Engineering* Vol. 132-136, Part 3, Trans Tech Publications, Switzerland, 1997.
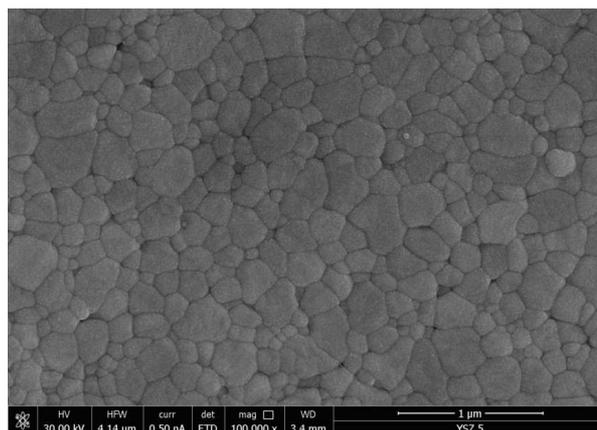5. M.M. Bućko, K. Haberko, M. Faryna, "Crystallization of

Figure 8. Microstructure of the sample 3.5YZ-5 sintered at 1400 °C in the dilatometer furnace
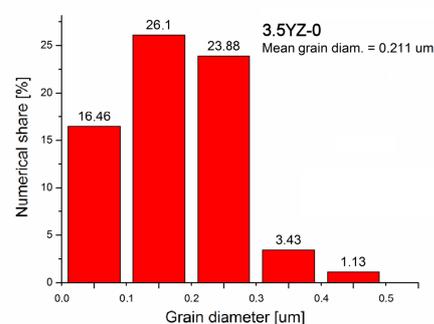

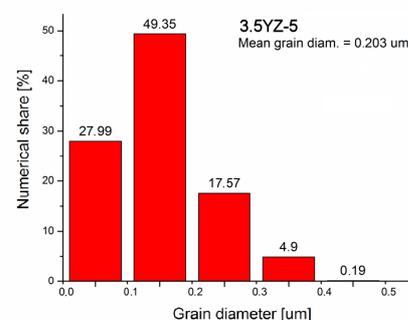**Figure 9. Grain size distribution of the sample 3.5YZ-0**

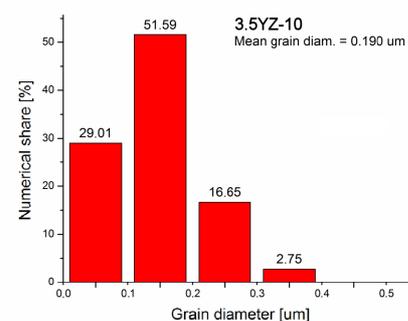**Figure 10. Grain size distribution of the sample 3.5YZ-5**

Figure 11. Grain size distribution of the sample 3.5YZ-10

zirconia under hydrothermal conditions", *J. Am. Ceram. Soc.*, **78** [12] (1995) 3397–3400.

6. R. Lach, M.M. Bućko, K. Haberko, M. Sitarz, K. Cholewa-Kowalska, "From nanometric zirconiapowder to transparent polycrystal", *J. Eur. Ceram. Soc.*, **34** [16] (2014) 4321–4326.

7. R. Lach, K. Wojciechowski, D. Zientara, K. Haberko, M.M. Bućko, "Zirconia nano-powder - a useful precursor to dense polycrystals", *Ceram. Int.*, **43** [5] (2017) 4470–4474.

8. K. Niihara, R. Morena, D.P.H. Hasselma, "Evaluation of K_{Ic} of brittle solids by the indentation method with low crack-to-indent ratios", *J. Mater. Sci. Lett.*, **1** (1982) 13–16.

9. K. Niihara, "A fracture mechanics analysis of indentation indentation induced Palmqvist crack in ceramics", *J. Mater. Sci. Lett.*, **2** (1983) 221–223.

10. Ł. Zych, K. Haberko, "Some observations on filter-pressing and sintering of zirconia nanopowder", *J. Eur. Ceram. Soc.*, **27** (2007) 867–871.