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PHYSICO-CHEMICAL PROPERTIES OF FINE-GRAINED POWDER IN Al_2O_3-ZrO_2 -Y_2O_3-CeO_2 SYSTEM PRODUCED BY COMBINED METHOD

At present due to the emergence of new methods of synthesising starting powders and their consolidation, Al_2O_3-based high-strength ceramic materials toughened by ZrO_2 (ZTA) are widely used as structural materials for various purposes. It is known that the material properties depend on the properties of the starting powders. Combined methods of powder preparation essentially extend the possibility to vary the powder properties. The purpose of this work is to produce a fine-grained powder of the composition (mol%) 58.5 α-Al_2O_3 - 41.5 ZrO_2 (Y_2O_3, CeO_2) by a combined method (hydro-thermal synthesis in an alkaline medium/mechanical mixing). The resultant fine-grained powder was heat-treated at 400, 550, 700, 850, 1000, 1150, 1300, and 1450°C with holding for 2 hours at each temperature. The properties of the synthesized powders were characterized by differential thermal analysis (DTA), scanning electron microscopy (SEM), X-ray diffraction (XRD) and specific surface measurements (BET). The microstructural and phase analyses were conducted by petrographic study. The powder morphology varies continuously topologically. The agglomerates after mechanical mixing had an irregular shape up to 1450°C. A tetragonal solid solution based on ZrO_2 (T - ZrO_2) and α-Al_2O_3 was identified in the powder after mechanical mixing. T-ZrO_2, as well as a monoclinic solid solution based on ZrO_2 (M-ZrO_2) and α-Al_2O_3 were identified after heating at 1450°C. The research results will be used for the microstructural design of ZTA composites.

Keywords: ZTA, nanocrystalline powder, fine-grained powder, solid solution based on ZrO_2, phase transition, microstructure design

WŁAŚCIWOŚCI FIZYKOCHEMICZNE DROBNOZIARNISTEGO PROSZKU W UKŁADZIE Al_2O_3-ZrO_2-Y_2O_3-CeO_2 WYTWARZANEGO METODĄ KOMBINOWANĄ

Obecnie, dzięki pojawieniu się nowych metod syntezy proszków wyjściowych i ich konsolidacji wysoko wytrzymałe materiały ceramiczne na bazie Al_2O_3 hartowane przez ZrO_2 (ZTA) są szeroko stosowane jako materiały konstrukcyjne do różnych celów. Wiadomo, że właściwości materiału zależą od właściwości wyjściowych proszków. Połączone metody przygotowania proszku w istotny sposób rozszerzają możliwość zmiany właściwości proszku. Celem tej pracy jest wytworzenie drobnoziarnistego proszku o składzie (% mol) 58,5 α-Al_2O_3 - 41,5 ZrO_2 (Y_2O_3, CeO_2) metodą łączoną (synteza hydrotermiczna w środowisku alkalicznym/mieszanie mechaniczne). Uzyskany drobnoziarnisty proszek poddano obróbce cieplnej w temperaturze 400, 550, 700, 850, 1000, 1150, 1300 i 1450°C z utrzymywaniem przez 2 godziny w każdej temperaturze. Właściwości zsyntetyzowanych proszków scharakteryzowano za pomocą różnicowej analizy termicznej (DTA), skaningowej mikroskopii elektronowej (SEM), dyfrakcji rentgenowskiej (XRD) i specyficznych pomiarów powierzchni (BET). Za pomocą badań petrograficznych przeprowadzono analizy mikrostrukturalne i fazowe. Morfologia proszku zmienia się w sposób ciągły topologicznie. Aglomeraty po mechanicznym mieszaniu miały nieregularny kształt do temperatury 1450°C. Tetragonalny stały roztwór oparty na ZrO_2 (T-ZrO_2) i α-Al_2O_3 został zidentyfikowany w proszku po mechanicznym mieszaniu. T-ZrO_2, jak również jednoskośny stały roztwór na bazie ZrO_2 (M-ZrO_2) i α-Al_2O_3 otrzymano po ogrzewaniu w temperaturze1450°C. Wyniki badań zostaną wykorzystane do mikrostrukturalnego projektowania kompozytów ZTA.

Słowa kluczowe: ZTA, proszek nanokrystaliczny, drobnoziarnisty proszek, stały roztwór na bazie ZrO_2, przemiana fazowa, projektowanie mikrostruktury

INTRODUCTION

Zirconia toughened alumina (ZTA) is a ceramic material based on Al_2O_3 where ZrO_2 is the toughening phase. ZTA ceramics have found broad applications on an industrial scale, such as cutting tools, tribo-components, biomedical implants and wear parts. ZTA ceramics are new generation materials and have been investigated for several decades [1, 2].

Currently, in ZTA composites few materials can be used: pure ZrO_2, Y_2O_3 stabilized ZrO_2 [3], CeO_2 stabilized ZrO_2 [4, 5], and Y_2O_3 with CeO_2 co-stabilized ZrO_2 [6-8]. Pure zirconia doped with yttrium and cerium oxides is used to increase the fracture toughness. ZTA composites which contain ZrO_2 (Y_2O_3, CeO_2) showed an increasing fracture toughness of up to 30%

compared to that of ZTA composites without the addition of CeO_2 [6].

The maximum increasing fracture toughness in ZTA occurs with the presence of both ZrO_2 - a tetragonal solid solution (T-ZrO_2) and ZrO_2 - a monoclinic solid solution (M-ZrO_2). The highest values of fracture toughness (8.38 MPa · $m^{0.5}$) and hardness (1688 HV) were obtained by a ZTA composite containing 5 wt.% CeO_2. The strength parameters of ZrO_2-based ceramics are determined by the transformation-toughening mechanism [1]. The properties of ZTA ceramics depend on the ability to control the phase transformation of T-ZrO_2 → M-ZrO_2 by controlling the composition and parameters of the technological process. The composition of a solid solution based on ZrO_2 for reinforcing an Al_2O_3 matrix should correspond to the T-ZrO_2 field of corresponding phase diagrams [7]. Analysis of the binary and ternary phase diagrams of systems that limit the Al_2O_3-ZrO_2-Y_2O_3-CeO_2 system showed that no mutual solubility of Al_2O_3 and ZrO_2 is found at temperatures below 1600°C. At the isothermal cross-section of the Al_2O_3-ZrO_2-Y_2O_3 phase diagram at 1500 and 1650°C, it is evident that, at the temperature of 1500°C, a single-phase tetragonal region of a zirconium-based solid solution exists in the range of up to 18 (mol%) CeO_2 and 3 (mol%) Y_2O_3. That is, yttrium aluminum garnets (YAG) are not formed at a content of Y_2O_3 up to 3 mol% [9, 10]. The main conclusion from the phase diagrams of limiting systems is that the Al_2O_3-ZrO_2 -Y_2O_3-CeO_2 system can be considered as a quasi-binary system of Al_2O_3 and a solid solution based on ZrO_2.

The properties of ZTA composites are largely determined by the properties of the starting powders and the methods of their consolidation. To achieve the required level of properties (strength and fracture toughness) in ZTA composites, the particles of the strengthening phase must be homogeneously distributed in the Al_2O_3 matrix. Soft-agglomerate powders with increasing sintering activity are required to create such composites. The properties of the starting powders are determined by the methods of their preparation [7]. Combined methods were preferred in order to obtain homogeneous powders during the last two decades. This makes it possible to control the powder characteristics at all stages of preparation [11-16]. Likewise, the optimized methods of nanocrystalline powder synthesis provide a high density of ZTA composites, a small amount of residual defects and strength characteristics.

One of the methods to achieve a fine-grained microstructure of ZTA composites is to reduce the sintering temperature. Therefore, introducing a ZrO_2 solid solution nanocrystalline powder- into the Al_2O_3-based matrix is effective. The mutual influence of the components on the phase transformations of each other is typical for such powders (as thermodynamically nonequilibrium systems). To minimize the possibility of developing a thermodynamically nonequilibrium system during heat treatment, α-Al_2O_3 powder should be used. This will reduce the impact of Al_2O_3 phase transformations on variation of the powder properties [2].

To obtain a a ZrO_2 solid solution nanocrystalline powder, it is effective to use hydrothermal synthesis in an alkaline medium. Among "wet" chemical methods, hydrothermal synthesis in an alkaline medium combines the advantages of sol-gel technology and co-precipitation, which allows one to achieve the maximum degree of homogeneity of the resulting powders. This method allows the morphology of the dispersed product to be controlled by varying the parameters of the process [7, 17]. Applying a mechanical influence in the process of obtaining fine-grained powders facilitates increasing their sintering activity. The method is simple, safe, accompanied by a minimum number of stages of precursor preparation, does not require complex chemical equipment or expensive reagents [2].

Therefore, the main objective of the present study is to investigate the variation of the physico-chemical properties of ZTA fine-grained powder, produced by a combined method, which consists of hydrothermal synthesis of ZrO_2 solid solution powder in an alkaline medium, followed by mechanical mixing with alumina powder, and to investigate the properties after thermal treatment in the temperature range 400÷1450°C. The composition of a solid solution based on zirconia (mol%) is 90 ZrO_2-8 CeO_2 - 2 Y_2O_3.

EXPERIMENTAL PROCEDURE

Materials

As the starting materials zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$), and cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) were used. α-Al_2O_3 powder (Baikalox 23810-1 produced by universal Photonics Incorporated, USA) with a specific surface area of 5 m^2/g was used. According to the BET data, it was established that the size of the α-Al_2O_3 powder particles is about 300 nm. All the agents were chemically pure.

Preparation of ZrO_2-based solid solution

ZrO_2-based solid solution nanocrystalline powder with the composition (mol%) 90 ZrO_2 - 8 CeO_2 - 2 Y_2O_3 was produced by hydrothermal synthesis in an alkaline medium.

During the synthesis co-precipitation was carried out from a mixture of aqueous solutions of the starting salts. An aqueous NH_4OH solution was used as the precipitant. Amphoteric zirconia and basis yttria and ceria enable the production of complex ZrO_2 - Y_2O_3 - CeO_2 powders only in alkaline conditions. The most suitable pH during the process was 8-9. The method of reverse deposition [18] was used, which allowed a high degree of homogeneity of the resulting mixture to be achieved, as a result of avoiding phased precipitation of the constituent hydroxides. The process was carried out

with constant stirring and subsequent boiling for 30 minutes for sediment aging. After boiling, translucent gel-like polymer complexes were formed, which were repeatedly decanted in distilled water. The degree of purification of the hydroxide sediment from chlorine ions was controlled by a qualitative reaction:

$$AgNO_3 + Cl^- \rightarrow AgCl \downarrow + NO_3^-$$

The absence of white sediment indicated the complete removal of chlorine ions, which is necessary to achieve a high degree of sintering activity of the resulting powder. The filtered precipitate was dried at 80°C for 24 hours in air. Hydrothermal treatment - the synthesis of nanocrystalline powder of a ZrO_2-based solid solution in alkaline medium - was carried out in a laboratory autoclave at a the temperature of 225°C for 4 hours. The pressure in the autoclave (1.6 MPa) corresponds to the pressure of the saturated vapor at this temperature. A transparent mother solution-nanocrystalline powder precipitate system was formed after processing. The powder was separated from the mother solution and dried at 80°C for 8 hours [18].

Preparation of Z42 nanopowder

Mechanical mixing of the α-Al_2O_3 powder with the hydrothermal nanocrystalline powder of the ZrO_2-based solid solution was performed in a ball mill for 8 hours. The mixing was performed in a ceramic drum with Al_2O_3 balls in an isopropyl alcohol medium. The mixture was dried at 80°C in air. The composition of mixed fine-grained powder is (wt.%) 58.5 α-Al_2O_3 - 41.5 ZrO_2 (Y_2O_3, CeO_2) (Z42).

Characterization

The resulting fine-grained powders were heat treated at temperatures of 400, 550, 700, 850, 1000, 1150, 1300 and 1450°C with a 2-hour holding time at each temperature to investigate the variation of the properties.

The processes occurring in the fine-grained powders during heat treatment were investigated by X-ray diffraction (XRD), differential thermal analysis (DTA), scanning electron microscopy (SEM) and nitrogen adsorption (BET). The XRD analysis was conducted using a DRON-3M powder diffractometer (Cu-K_α-radiation, Ni-filter). The scan rate varied from 1 to 4°/min. To clarify the centers of the peaks and other parameters, the peaks in the obtained diffractograms were approximated as Voigt and Gauss functions. The differences for the reflections of zirconium dioxide peaks were insignificant. The phase composition was determined using the Match program. Standard data were used from the PDF-2 database. The crystallite sizes were calculated by the Scherrer equation. A scanning electron microscope with an REM 106Y energy micro analyzer (carbon film was sprayed on the powder samples) was employed. The specific surface area of the powders was determined by BET (Sumperk, Slovakia). DTA was conducted using a derivatograph Q-1500 (F. Paulik, J. Paulik, L. Erday system; made in Hungary, the heating rate of the samples was 10°C/min). The microstructural and phase analyses were conducted by petrographic study using a MIN-8 microscope with a standard set of immersion liquids (magnification 60÷620).

RESULTS AND DISCUSSION

Properties of initial powder

The phase composition of the powder was determined by two methods: X-ray analysis and microstructural analysis (performed by petrography). The microstructural analysis showed that in the initial fine-grained α-Al_2O_3 powder anisotropic soft agglomerates of round and irregular shapes were formed. After hydrothermal synthesis in the alkaline medium in the powder of the hydrothermal ZrO_2-based solid solution two types of isotropic agglomerates were formed: (1) fine-grained agglomerates of high-relief grains, the size of which is beyond the resolution of the microscope and (2) transparent agglomerates of an irregularly fragmented form, the boundaries of which are layers of a fine-grained phase.

According to the microstructural analysis (performed by petrography), a dispersed mixture was formed after mechanical mixing, and the particle sizes of the mixture were beyond the resolution of the microscope. All the Al_2O_3 particle agglomerates were coated with a fine-grained ZrO_2 phase with high grain relief.

Petrography studies showed that the Z42 powder contains α-Al_2O_3 and a tetragonal ZrO_2-based solid solution (T-ZrO_2) during heat treatment. The conclusion is based on the fact that Z42 powder contains only anisotropic regions (α-Al_2O_3 and T-ZrO_2). The amount of anisotropic grains with high relief increases with subsequent heat treatment. Traces of M-ZrO_2 after heat treatment in the temperature range of 1300÷1450°C were determined exclusively on the basis of X-ray results (according to the crystal optical characteristics, M-ZrO_2 and T-ZrO_2 are anisotropic).

According to the X-ray analysis α-Al_2O_3 and a T-ZrO_2 - based solid solution were identified in the initial fine-grained powder after mechanical mixing (Fig. 1). The thermal analysis results of the Z42 fine-grained powder before heat treatment is shown in Figure 2.

There are two obvious effects on the DTA curve: endothermic with a minimum at 90°C and exothermic with a maximum at 260°C. The endothermic effect on the DTA curve with a minimum at 90°C is correlated with the corresponding broad effect on the DTG curve. This effect is associated with the removal of adsorbed water. The weight change rate of the sample is maximum up to 130÷140°C. The total weight loss in the

specified range is up to 2%. After that, the weight loss rate slows down, and the process continues to 420°C. The total weight loss in this range is 3.5%. The exothermic effect with the maximum at 260°C is observed on the DTA curve and apparently is associated with crystallization of the phase, which remained after hydrothermal synthesis.

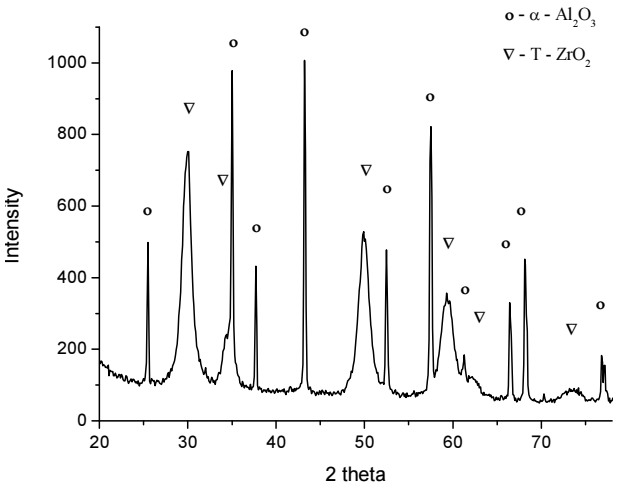

Fig. 1. XRD pattern of Z42 initial powder

Rys. 1. Dyfraktogram wyjściowego proszku Z42

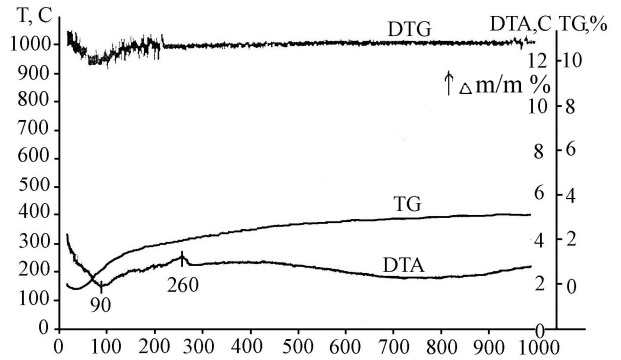

Fig. 2. Thermal analysis of fine-grained Z42 powder before heat treatment

Rys. 2. Wyniki analizy termicznej drobnoziarnistego proszku Z42 przed obróbką cieplną

The specific surface areas of the α-Al_2O_3 powder and ZrO_2-based solid solution hydrothermal powder (mol%) 90 ZrO_2 - 8 CeO_2 - 2 Y_2O_3 were 5 and 94 m^2/g, respectively. The specific surface area of the fine-grained Z42 powder was 57 m^2/g. The morphology of the initial powders is shown in Figure 3.

The ZrO_2-based solid solution hydrothermal powder contains spherical and irregularly shaped agglomerates. The spherical agglomerates have almost the same size ~ 20 μm. It is clearly seen (Fig. 3a) that they consist of conglomerates of primary particles up to 5 μm. Single irregularly shaped agglomerates reach the size of 20 μm, but the main fraction of agglomerates is in the range of 5÷10 μm in length. These agglomerates also contain conglomerates of primary particles.

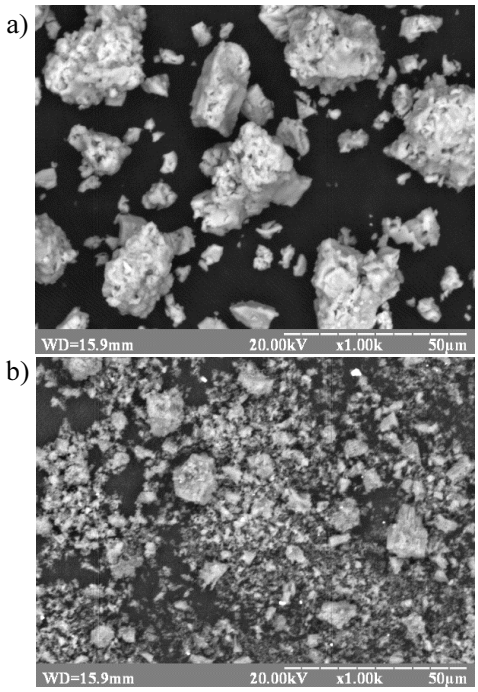

Fig. 3. Morphology of ZrO_2-based solid solution hydrothermal powder (a) and α-Al_2O_3 powder (b)

Rys. 3. Morfologia proszku ZrO_2 na osnowie roztworu stałego proszku hydrotermalnego (a) oraz proszku α-Al_2O_3 (b)

The α-Al_2O_3 powder (Fig. 3b) contains 5% round-shaped agglomerates with a diameter of ~10÷15 μm. The main fraction is agglomerates in the range from 1 to 5 μm. In this case, the agglomerates are not monolithic either, and consist of conglomerates of primary particles. In Z42 powder soft agglomerates of an irregular shape, up to 20 microns, were formed.

The morphology of the initial Z42 powder is shown in Figure 4.

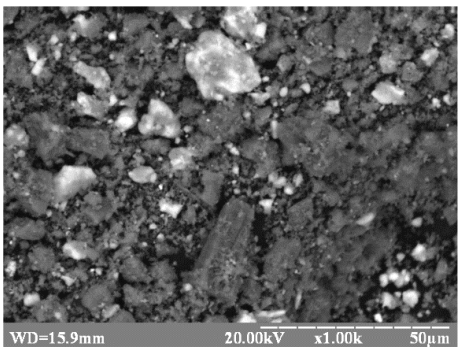

Fig. 4. Morphology of initial Z42 powder

Rys. 4. Morfologia wyjściowego proszku Z42

Variation of powder physico-chemical properties during thermal processing

The XRD results of Z42 thermal treatment are presented in Table 1.

The phase composition of the powder practically did not vary during thermal treatment in the temperature range 400÷1150°C: α-Al_2O_3 and a tetragonal solid solution based on ZrO_2 (T- ZrO_2) remained (Table 1). After

heat treatment at 1300 and 1450°C, α-Al_2O_3 and a mixture of two solid solutions based on ZrO_2 (T-ZrO_2 and M-ZrO_2) were indicated in the powder.

TABLE 1. **XRD results of Z42 thermal treatment**
TABELA 1. **Wyniki XRD Z42 poddanego obróbce cieplnej**

T [°C]	Z42 phase composition
400	α-Al_2O_3 + T- ZrO_2
550	α-Al_2O_3 + T -ZrO_2
700	α-Al_2O_3 + T -ZrO_2
850	α-Al_2O_3 + T-ZrO_2
1000	α-Al_2O_3 + T-ZrO_2
1150	α-Al_2O_3 + T-ZrO_2
1300	α-Al_2O_3 + T-ZrO_2, traces of M-ZrO_2
1450	α-Al_2O_3 + T-ZrO_2, traces of M-ZrO_2

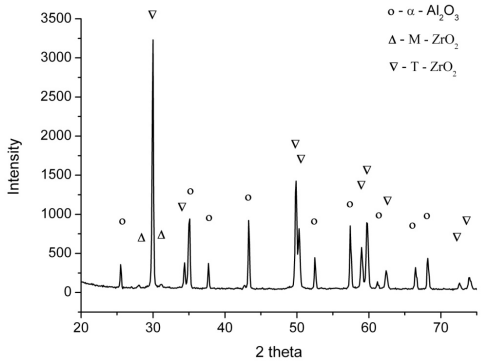

Fig. 5. XRD patterns of Z42 fine-grained powder after heat treatment at 1450°C

Rys. 5. Dyfraktogram drobnoziarnistego proszku Z42 po obróbce cieplnej w temperaturze 1450°C

The changes in the size of the primary particles of a ZrO_2-solid solution according to the Scherrer equation are presented in Figure 6. The applied temperature range of thermal treatment can be divided into sections, which was characterized by different rates of structural changes - the growth of crystallite size. A slight increase in crystallite sizes was observed after thermal treatment in the ranges of 400÷850 and 1300÷1450°C (Fig. 6).

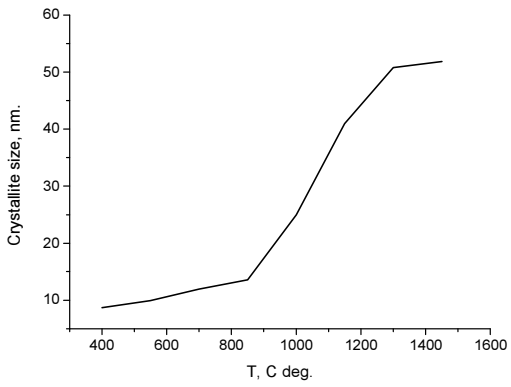

Fig. 6. Changes in crystallite size of ZrO_2- solid solutions after heat treatment in 400÷1450ºC range

Rys. 6. Zmiany w wielkości krystalitów roztworu stałego ZrO_2 po obróbce cieplnej w zakresie temperatur 400÷1450ºC

A relatively high growth rate exists in the temperature range of 850÷1300°C. The main diffraction patterns corresponding to the low-temperature range are shown in Figure 7.

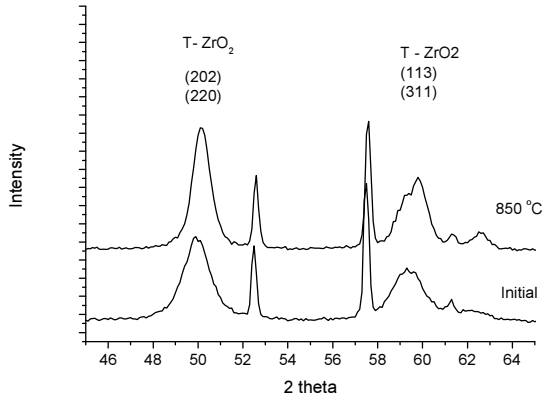

Fig. 7. XRD patterns of initial Z42 fine-grained powder and after heat treatment at 850°C

Rys. 7. Dyfraktogram wyjściowego drobnoziarnistego proszku Z42 oraz po obróbce cieplnej w temperaturze 850°C

It is clear that due to the small size of the crystallites, the pairs of peaks (202) - (220) and (113) - (311) are wide and merge. The shape of the peaks changes with increasing the temperature - the half-width value decreases and the peak height increases. This reflects the growth of crystallites. Diffraction patterns of a high-temperature region are shown in Figure 8.

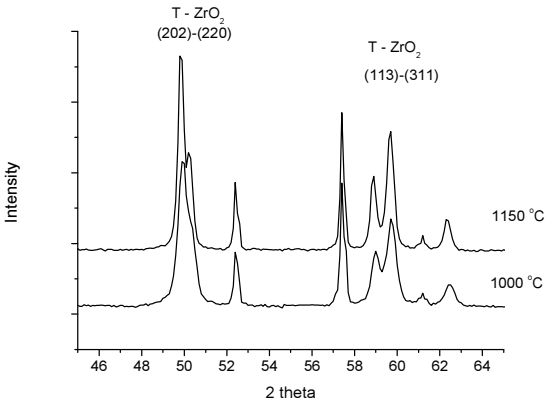

Fig. 8. XRD patterns of fine-grained Z42 powder after heat treatment at 1000ºC and 1150°C

Rys. 8. Dyfraktogram drobnoziarnistego proszku Z42 po obróbce cieplnej w temperaturach 1000 i 1150°C

The changes in the specific surface area of fine-grained Z42 powders after heat treatment in the range from 400 to 1450°C are shown in Figure 9. It can be seen that the variation of the Z42 fine-grained powder specific surface area corresponds to the crystallite size changes of the ZrO_2-solid solution during thermal treatment (Fig. 6) and the sintering processes that occur with the increasing temperature. The bend at 850°C can be explained by the beginning of sintering of freely poured powder and the bend at 1450°C - with completion of the sintering processes.

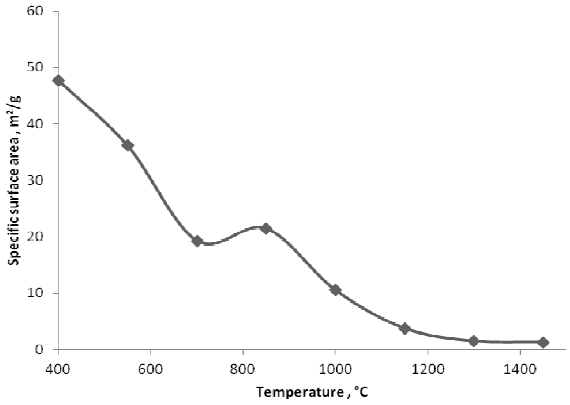

Fig. 9. Changes in specific surface area of fine-grained Z42 powders after heat treatment in 400÷1450°C range

Rys. 9. Zmiany w powierzchni właściwej drobnoziarnistych proszków Z42 po obróbce cieplnej w zakresie temperatur 400÷1450°C

The morphology of the fine-grained Z42 powders after heat treatment is shown in Figure 10.

We can conclude that the morphology of the Z42 powders changes topologically with no interruption. Agglomerates of an irregular shape were formed after mechanical mixing and the shape was maintained after the heat treatment, but the average size of the agglomerates was reduced to 5÷10 μm. The fraction of agglomerates up to 5 μm increased after heat treatment of the powder. Further sintering of freely poured powders is accompanied by decreasing the agglomerate sizes and the formation of agglomerate bonds. With increasing the temperature of thermal treatment up to 1300÷1450°C, the size of the agglomerates decreases, and compact agglomerates are formed, which form sintered chain-like conglomerates.

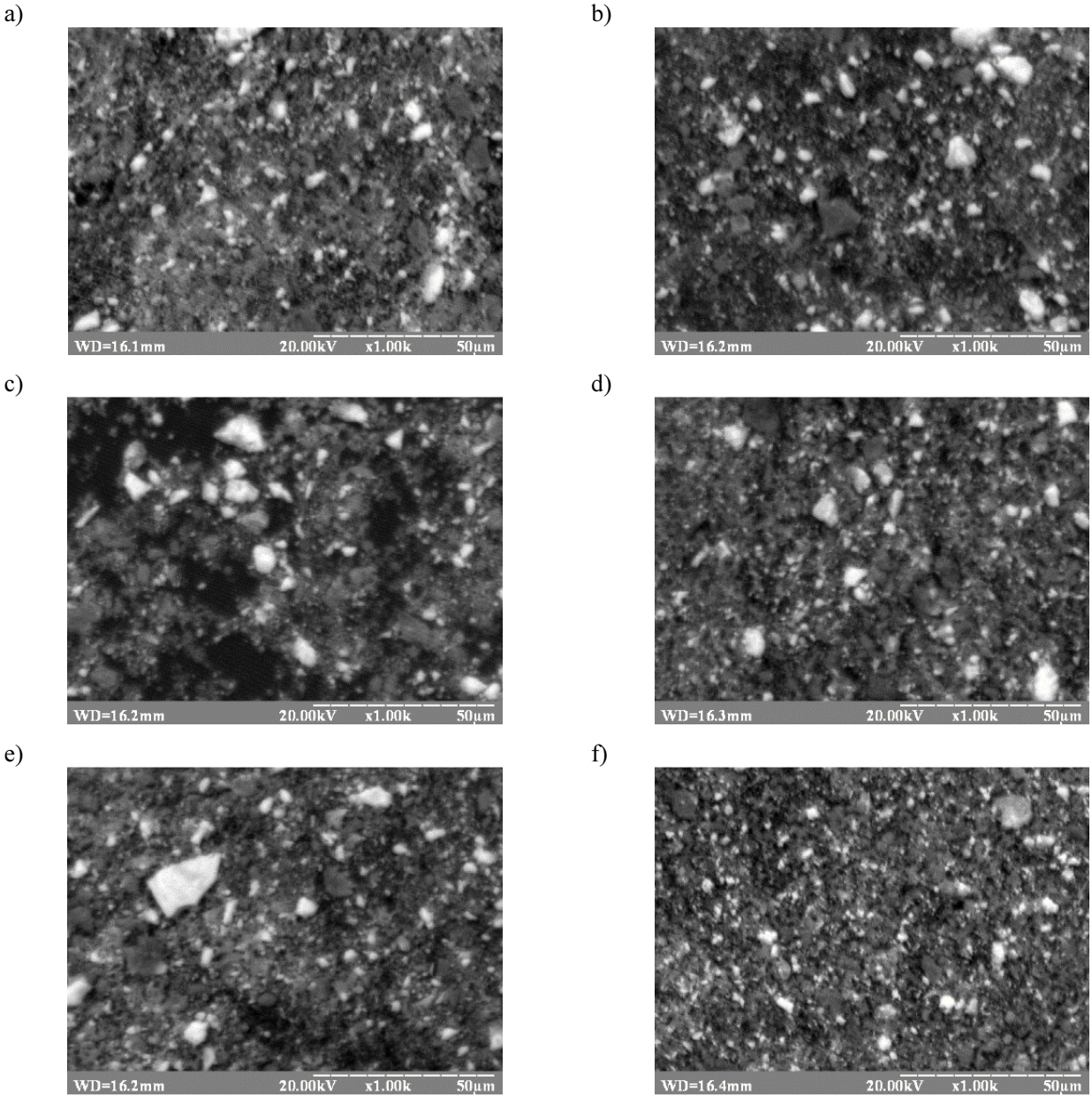

Fig. 10. Morphology of fine-grained Z42 powders after heat treatment at 400 (a), 850 (b), 1000 (c), 1150 (d), 1300 (e), 1450°C (f)

Rys. 10. Morfologia drobnoziarnistych proszków Z42 po obróbce cieplnej w temperaturze 400 (a), 850 (b), 1000 (c), 1150 (d), 1300 (e), 1450°C (f)

CONCLUSIONS

ZTA powder of the composition (wt.%) 58.5 α-Al_2O_3 - 41.5 ZrO_2 (Y_2O_3, CeO_2) was produced by a combined method of hydrothermal synthesis in an alkaline medium and mechanical mixing. The variations of the powder properties after production and thermal treatment in the range from 400°C to 1450°C were investigated. A tetragonal solid solution based on ZrO_2 and α-Al_2O_3 were identified in the powder after mechanical mixing. T-ZrO_2, as well as a monoclinic solid solution based on ZrO_2 and α-Al_2O_3 were identified after thermal treatment at 1450°C.

The powder morphology varies continuously topologically. The agglomerates after mechanical mixing and until 1450°C had an irregular shape. With the increasing the temperature of thermal treatment up to 1300÷1450°C, the agglomerate sizes decreased, confirming the conclusion about the intensification of powder sintering.

These results offer possibilities for the microstructural design of high-performance ZTA composites with a fine-grained structure at low sintering temperatures. The variation of the processing temperature of the starting powders and the use of various methods of consolidation allow the creation of composites with different types of microstructures for structural ceramics and ceramics for medical purposes.

REFERENCES

[1] Hannink R.H.J., Kelly P.M., Muddle B.C., Transformation toughening in zirconia - containing ceramics, J. Am. Ceram. Soc. 2000, 83, 3, 461-487.

[2] Dudnik E.V., Tsukrenko V.V., Glabai M.S., Ruban A.K., Red'ko V.P., Khomenko A.I., Nanocrystalline powders in ZrO_2–Y_2O_3–CeO_2–Al_2O_3–CoO system for microstructural design of ZrO_2-bazed color composites, Powder Metallurgy and Metal Ceramics 2017, 56, 7-8, 407-415.

[3] Chevalier J., Deville S., Munch E., Jullian R., Critical effect of cubic phase on aging in 3 mol% yttria-stabilized zirconia ceramics for hip replacement prosthesis, Biomaterials 2004, 25, 5539-5545.

[4] Kumar P.A., Biswas K., In vitro cytocompatibility, ageing and wear behavior of ceria stabilized zirconia bioceramic, Ceram. Intern. 2014, 40, 15889-15895.

[5] Ponnilavan V., Kannan S., Structural, morphological and mechanical characteristics on the role of excess ceria additions in zirconia toughened alumina systems, Journal of Alloys and Compounds 2017, 694, 1073-1082.

[6] Rejab N.A., Zahirani A., Azhar A., Ratnam M.M., Ahmad Z.A., The effects of CeO_2 addition on the physical, microstructural and mechanical properties of yttria stabilized zirconia toughened alumina (ZTA), Int. J. Refract. Met. Hard Mat. 2013, 36, 162-166.

[7] Dudnik E.V., Shevchenko A.V., Ruban A.K., Redko V.P., Lopato L.M., Microstructural design of ZrO_2–Y_2O_3–CeO_2–Al_2O_3 materials, Powder Metallurgy and Metal Ceramics 2011, January 49, 528-536.

[8] Naga S.M., Abdelbary E.M., Awaad M., Effect of the preparation route on the mechanical properties of yttria-ceria doped tetragonal zirconia. Ceram. Intern. 2013, 39, 2, 1835-1840.

[9] Lakiza S.N., Lopato L.M., Stable and metastable phase relations in the system alumina-zirconia-yttria, J. Am. Ceram. Soc. 1997, 80, 4, 893-902.

[10] Lopato L.M., Andrievskaya E.R., Interaction of cerium oxide with hafnium, zirconium, and yttrium oxides at 1500°C, Powder Metallurgy and Metal Ceramics 2001, 40, 405-413.

[11] Palmero P., Naglieri V., Chevalier J., Fantozzi G., Montanaro L., Alumina based nanocomposites obtained by doping with inorganic salt solution: application to immiscible and reactive system, J. Europ. Ceram. Soc. 2009, 29, 59-66.

[12] Naglieri V., Joly-Pottuz L., Chevalier J., Lombardi M., Montanaro L., Follow-up of zirconia crystallization on a surface modified alumina powder, J. Europ. Ceram. Soc. 2010, 30, 3377-3387.

[13] Sommer F., Landfried R., Kern F., Gadow R., Mechanical properties of zirconia toughened alumina with 10-24 vol.% 1.5 mol% Y-TZP reinforcement, J. Europ. Ceram. Soc. 2012, 32, 3905-3910.

[14] Palmero P., Sola A., Naglieri V., Bellucci D., Lombardi M., Cannillo V., Elaboration and mechanical characterization of multi-phase alumina-based ultra-fine composites, J. of Material. Scien. 2012, 47, 1077-1084

[15] Naglieri V., Palmero P., Montanaro L., Chevalier J., Elaboration of alumina-zirconia composites: Role of the zirconia content on the microstructure and mechanical properties, Materials 2013, 6, 2090-2102.

[16] Palmero P., Montanaro L., Reveron H., Chevalier J., Surface coating of oxide powders: A new synthesis method to process biomedical grade nano-composites, Materials 2014, 7, 5012-5037.

[17] Shigeyuki Sōmiya, Tokuji Akiba, Hydrothermal zirconia powders: A bibliography, J. Europ. Ceram. Soc. 1999, 19, 81-87.

[18] Dudnik E.V., Shevchenko, Variation in properties of ZrO_2–Y_2O_3–CeO_2–Al_2O_3 powders during thermal treatment at 400 to 1300°C, Powder Metal. Met. Ceram. 2010, 49, 125-134.

