Arch. Metall. Mater. **62** (2017), 4, 2045-2049

DOI: 10.1515/amm-2017-0303

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MICROSTRUCTURE CHARACTERIZATION OF COMPOSITE FROM ZrO_2 – Ti SYSTEM

In this work the microstructure analysis of composite from ZrO_2 – Ti system were presented. For the preparation of the composite samples nanometric ZrO_2 powder stabilized by 3 mol% of Y_2O_3 and micrometric titanium powder were used. The composites with 10 vol.% addition of titanium particles were prepared by slip casting method. The sintering process was conducted at 1450°C with 2 hours' dwell time, in the inert atmosphere of argon. The microstructure observations were carried out with the use of SEM and STEM microscopes. The quantitative analysis and stereological characterization were performed. The SEM and STEM observations allowed characterizing the microstructure of composite samples. Especially, the interface between titanium particles and zirconia matrix was described. The growth of the zirconia grains around the Ti rich areas was observed. The increase of the zirconia grains size results from the reaction on the interface between titanium particle and zirconia matrix during the sintering process.

Keywords: titanium, zirconium oxide (ZrO_2), composite, stereology

1. Introduction

In preparation of the composite materials, there are many technological problems, especially with obtaining the proper bonding between components. The selection of technology and the components affect the quality and properties of the final materials. Moreover, often the components of composite materials are characterized by high individual activity what result in reaction during the formation process with or without creation the new phase. All of these issues predetermine the optimal properties and in results the future applications of the final composite materials [1,2].

Ceramic – metal composites are widely investigated and developed because of the interesting properties and possible applications in many types of industry. The composites from zirconia – titanium system with zirconia matrix and titanium particles are the example of ceramic-metal composite, which represented a complex structure [3,4].

The zirconium dioxide (ZrO_2) stabilized by 3 mol% of yttrium oxide (Y_2O_3) is characterized by high fracture toughness, high thermal shock resistance, high corrosion resistance and biocompatibility [5,6]. Titanium is the metal which characterized by high corrosion resistance and biocompatibility. Due to the high melting point (1667°) and the similar coefficient of thermal expansion to zirconia, titanium is a good candidate for the preparation of the zirconia matrix composite with metal particles [7].

The microscopic observations of composites microstructure are useful to investigate the activity between components in the zirconia – titanium system. For example, the partial solubility of titanium along the grain boundaries of ZrO_2 without creation of the new phase was found on the based on many studies [8-10]. Webber at al. [9] showed the partial limited solubility of Ti into ZrO_2 and the effect of the blackening of zirconia through the formation of oxygen deficiencies [9]. The research conducted by Ruh [10] showed that the maximum quantity of titanium was dissolved in the ZrO_2 in an amount about 4 at.%. Conversely, up to 10 mol% of ZrO_2 was dissolved in the Ti [10].

Lin et al. [11-13] conducted several studies on the diffusion reactions between zirconia and titanium annealed at temperatures between 1100°C and 1550°C. In this work, after annealing the conditions of the formation the new phases and the types of changes, which occurred after heating, was determined. In addition, the grain growth according to the transformations was observed. The mechanism affecting on the grain growth was connected with the forming of the oxygen deficiencies in the zirconia by passing the oxygen to titanium [11-13].

There is still no comprehensive research, which describe the microstructure of composites from ZrO_2-Ti system. Therefore, the aim of this work was to characterize of the microstructure of composite ZrO_2 – 10% vol. Ti, prepared by slip casting method and sintered at temperature 1450°C in the inert argon atmosphere. The microstructure observations were conducted with using the scanning electron microscopy and transmission electron microscopy. Based on the SEM and STEM images the characterization of microstructure was done. The size of the ZrO_2 grains and the precipitation in the composite were investigated.

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2. Experimental details

In this work, the commercially available powders of zirconia and titanium were used. In the preparation of the composites the nano-sized powder of zirconium oxide ZrO_2 stabilized by 3 mol% Y_2O_3 (TOSOH, Japan) with particle diameter below 100 nm and a density of 5.88 g/cm^3 and the micrometer titanium powder (MerckChemicals, Germany) with particle diameter about 10.8 ± 2.9 μm and a density of 4.4 g/cm^3 were used. The density of powders was measured on a helium pycnometer Accu Pyc II 1340.

For the preparation of the composites samples, the slip casting method was used. The scheme of the forming method was showed in the Fig. 1.

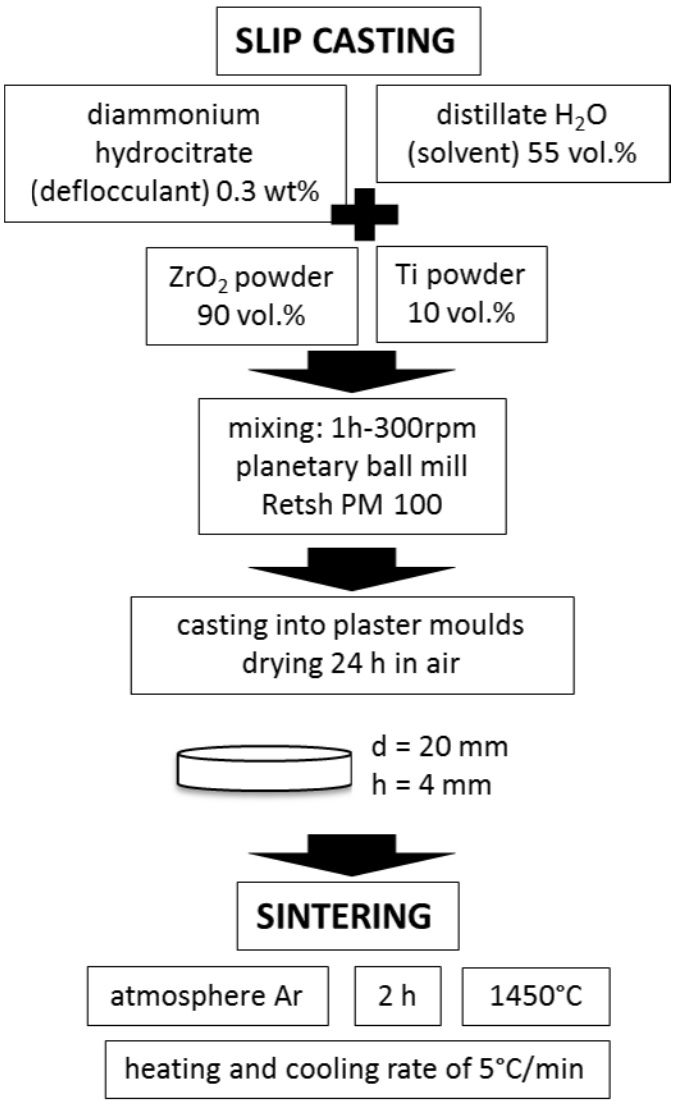

Fig. 1. Scheme of the ZrO_2 – 10 vol.% Ti composite formation

The microstructure analysis was conducted on the cross section of composite samples. The samples were polished by ion milling system IM – 4000. Prepared samples were observed with the scanning electron microscopy HITACHI SU-8000 worked with the backscattered electron imaging (BSE). The microstructure of bonding between the Ti particles and ceramic matrix was investigated using the scanning transmission electron microscopy HITACHI STEM HD 2700, which operated at an accelerating voltage of 200 kV. The sample for observation was prepared by scanning ion microscopy HITACHI NB-5000 according to the procedure [14]. Based on the microscopic pictures the stereological analysis was conducted using the computer program MicroMeter [15]. The image was processed in order to identify and characterize the morphology of ZrO_2 matrix and size of new phase precipitations. In the analysis, the parameter as an equivalent diameter (diameter of a circle having the same area as the surface of the grain or the precipitation) was used. Moreover, the X-ray phase composition analysis was done using X-ray diffraction on a Rigaku MiniFlex II diffractometer using Cu Kα of wavelength λ = 1.54178 Å. Terms of records: voltage 30 kV, current 15 mA, angular range 2Theta 20°-100°, step 0.02° and counting time 0.5 s.

3. Results and discussion

The results of X-ray analysis (Fig. 2) revealed existing in composite two phases: tetragonal ZrO_2 and titanium rich phase, which includes oxygen and zirconium.

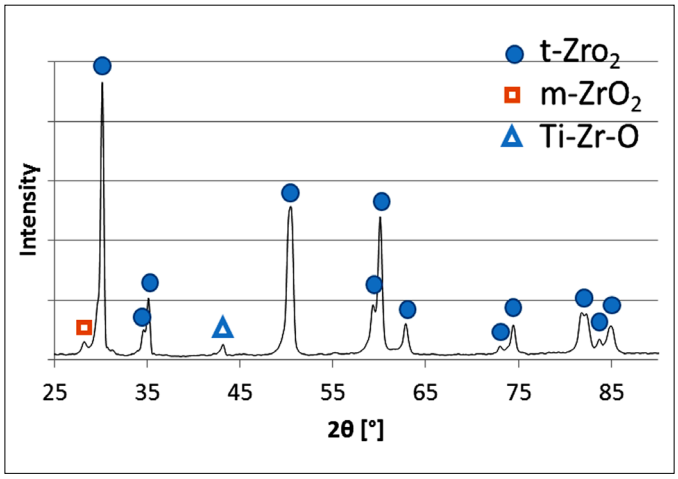

Fig. 2. X-Ray diffraction spectra of the cross section of ZrO_2 + 10 vol.% Ti composite

The microstructure of ZrO_2 – 10 vol.% Ti composite was showed in the Fig. 3. The Ti-rich areas and their aggregates in the ceramic matrix were found. The observations indicated no large agglomerates of Ti-rich areas, which confirmed the good homogenisation of the powder mixture before slip casting process. The equivalent diameter of Ti-rich areas was 7.8 μm ± 5.5 μm which was significantly smaller than the average size of the starting titanium powder. This value of equivalent diameter was the result of the fragmentation of the unstable agglomerates of metallic powder during the mixing in the planetary ball mill. Moreover, the final size of Ti-rich areas is controlled by diffusion process, both Ti into ZrO_2 and Zr into Ti.

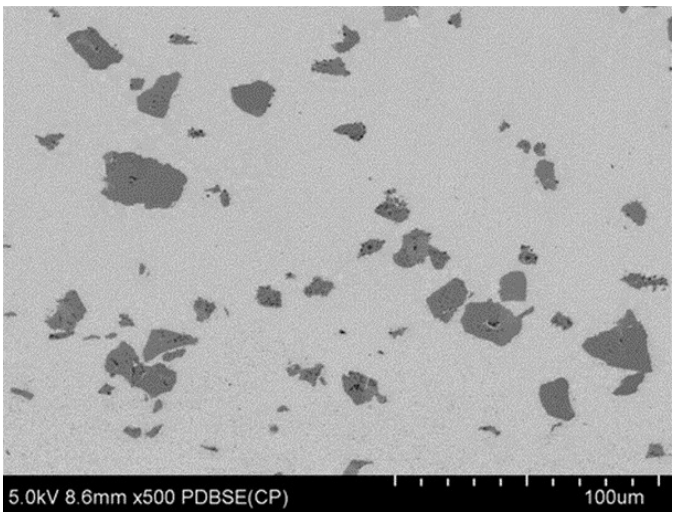

Fig. 3. Microstructure of ZrO_2 – 10 vol.% Ti composite (dark contrast-Ti, bright contrast – ZrO_2), SEM

Fig. 4 showed the Ti-rich areas in the zirconia matrix with characteristic voids inside these areas which may arise from the release of hydrogen from the titanium particles present in powder residue from the manufacturing process. As a very characteristic feature of ZrO_2-Ti couples, the significant grain growth of ZrO_2 grains around the Ti-rich areas was observed (Fig. 5). With the increasing distance from the Ti/ZrO_2 interface the zirconia grains decreases. The existing of various sizes of zirconia grains affected the allocation of grains into two zones: I – the zone of the large zirconia grains and II – zone of the smaller zirconia grains. Additionally, the dark precipitations on the zirconia grain boundaries were observed.

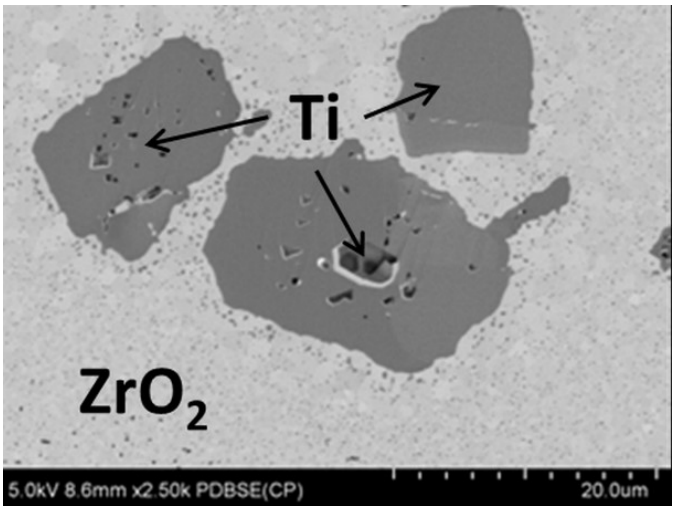

Fig. 4. Microstructure for selected Ti-rich areas in the ZrO_2 – 10 vol.% Ti composite, SEM

During the analysis of ZrO_2 grains size two zones can be distinguished: I – the large zirconia grains around the Ti-rich areas and II – the smaller zirconia grains located further from the Ti/ZrO_2 interface. The stereological analysis was presented in the Fig. 6 and Fig. 7. The equivalent diameter for the large ZrO_2 grains (zone I) was about 1.2 μm. The analysis of the ZrO_2 grains situated further away from the titanium – zirconia interface (zone II) revealed that the grain size distribution was closer to the Gauss distribution. The average diameter of the zirconia grains in this zone was 0.5 μm and the majority amount of zirconia grains were in the range of 0.4-0.8 μm.

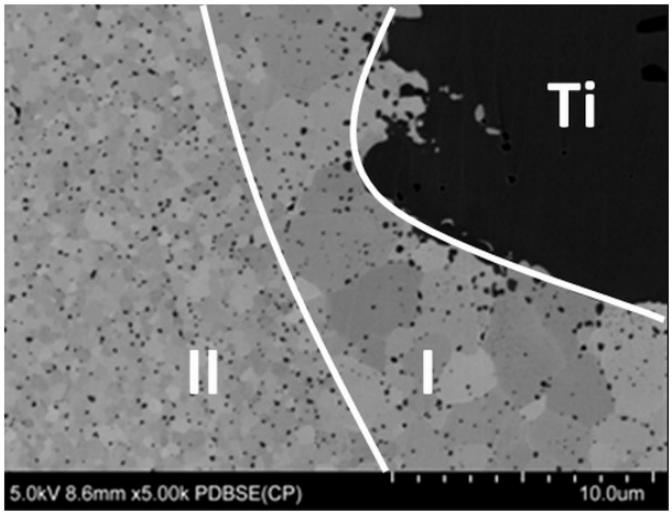

Fig. 5. Microstructure of the ZrO_2 – 10 vol.% Ti composite on the Ti/ZrO_2 interface, SEM

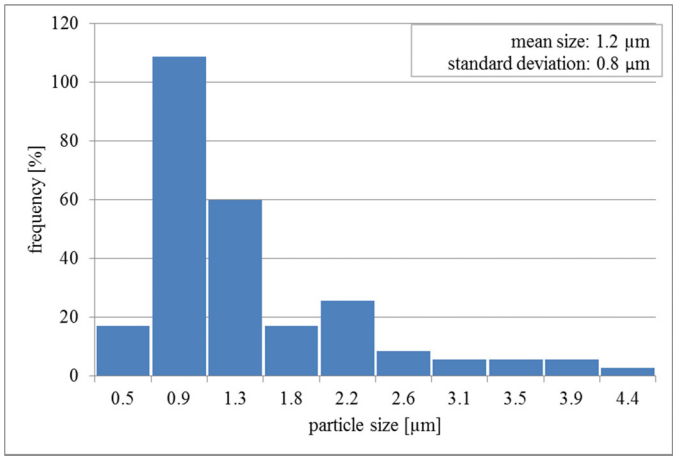

Fig. 6. Analysis of the ZrO_2 grain size in the zone I (frequency N [%] against diameter d_2 [μm])

The microstructure of the ZrO_2 – 10 vol.% Ti composite made using the STEM was presented in the Fig. 8. The observation of surrounding Ti-rich areas confirmed the significant growth of zirconia grains. The amount of the large zirconia grains decreased with the increasing of distance from the interface of Ti/ZrO_2, which may result from the limited diffusion of titanium into ceramic matrix. The zirconia grains around the titanium particle interacted directly with metal particle. The following reaction leaded to make the oxygen deficient in the zirconia. A significant amount of oxygen diffused and dissolved into titanium. The result of this reaction activated the grain growth. In opposite direction the diffusion of the titanium into ceramic

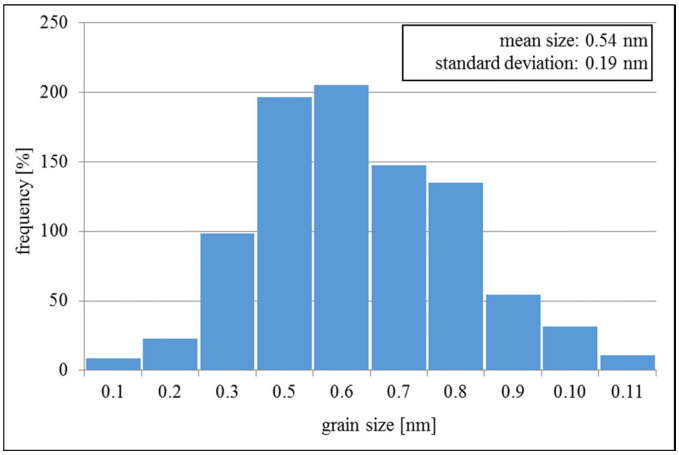

Fig. 7. Analysis of the ZrO_2 grain size in the zone II (frequency N [%] against diameter d_2 [μm])

matrix along the zirconia grain boundaries was observed. The chemical analysis of the precipitation areas was carried out and showed in the Fig. 9. The large specific surface area of used zirconia nanoparticles could intensify the reactions occurring between zirconium oxide and titanium. It was found that the precipitation mostly exist in the triple point of zirconia grain boundaries. However, also some precipitations are located at the zirconia grain boundaries. The appearing precipitations were rich in the titanium, zirconium and oxygen. The EDS analysis of this selected area confirmed the diffusion of the titanium, zirconium and the oxygen in the both directions. The diffusion of titanium into zirconia matrix was associated with the reaction between titanium and zirconium that mean the partial dissolution of zirconium and oxygen in diffusing titanium. The new phase was based on the titanium and was rich in zirconium and oxygen, which could be describe as Ti(Zr,O) and was detected at X-ray diffraction analysis. Determining the crystallographic structure of the new phase requires the additional studies, which are in progress.

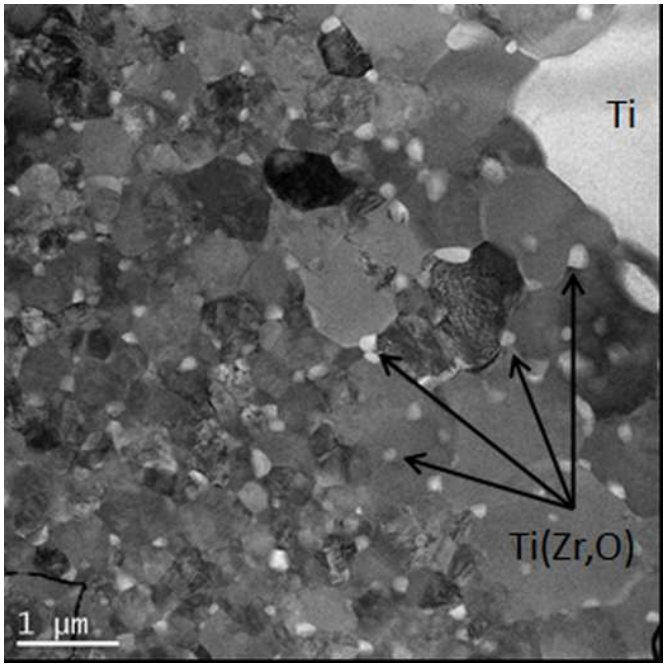

Fig. 8. Microstructure of ZrO_2 – 10 vol.% Ti composite on the interface between Ti particle – ZrO_2 matrix, STEM

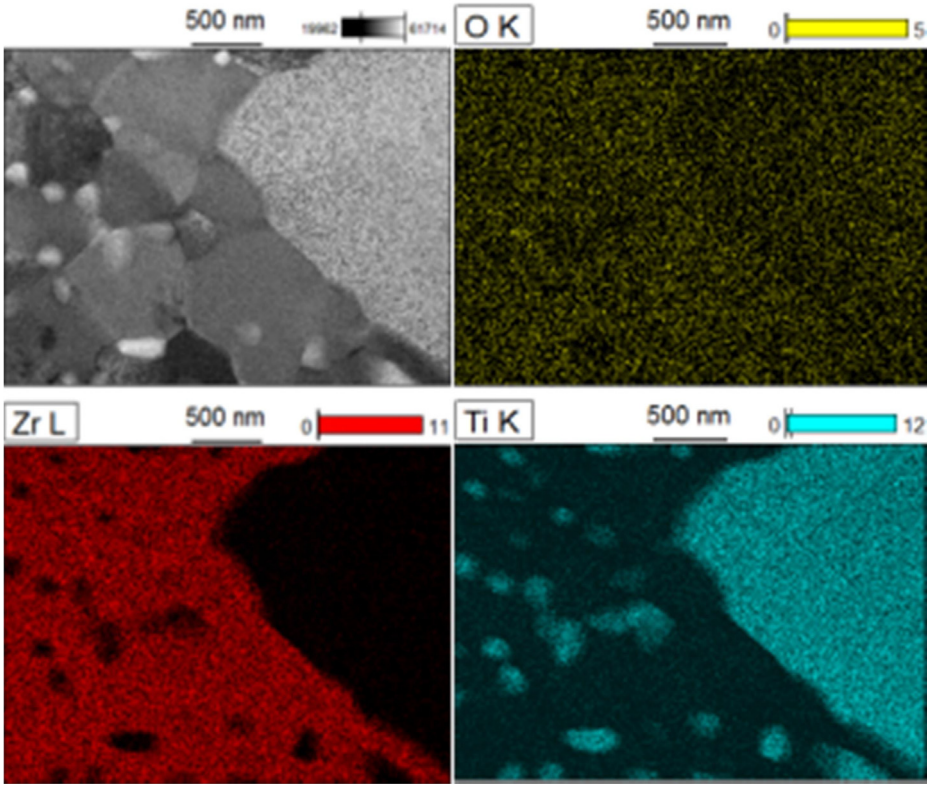

Fig. 9. SEM – EDS element distribution maps of Zr, Ti and O in the ZrO_2 – 10 vol.% Ti composite at the interface between Ti particle– ZrO_2 matrix

Based on the TEM pictures the analysis of the size of the new phase Ti(Zr,O) precipitates was made (Fig. 10). The equivalent diameter of the new phase precipitates was 152.6 nm. The existence on the new phase Ti(Zr,O) precipitates could effected on the properties of the formed composite material.

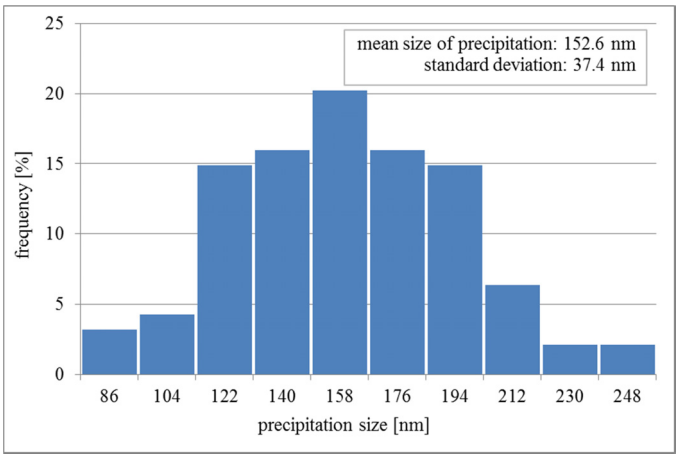

Fig. 10. Distribution of the precipitation size on the growth ZrO_2 grains near the Ti particle – ZrO_2 matrix interface (frequency N [%] against diameter d_2 [μm])

4. Conclusion

The ceramic-metal composites from ZrO_2 – Ti system were characterized by complex microstructure, which was confirmed by microscopic observations. The intensive diffusion of elements: Zr, Ti and O leads to creation a new phase Ti(Zr, O) which is located as separated areas and precipitations at zirconia grain boundaries. The TEM microstructure observations allowed for conclusion that the new titanium-based phase precipitates rich in zirconium and oxygen – Ti(Zr,O) were occurred along the zirconia grains boundaries. The precipitates were characterized by small size – the average diameter was about 150 nm. The reaction between components created a characteristic area of large grains of zirconia around the titanium particles. The change of grain size on the border between Ti particle and ZrO_2 matrix was described in two zones of large and small ZrO_2 grains and it was confirmed by stereological analysis.

Acknowledgements

The work was done in frame of the project financed by National Center of Science (NCN), project DEC-2013/11/B/ ST8/00309.

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