NANOCOMPOSITES IN THE ZrO_2-Al_2O_3-WC SYSTEM

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Abstract
Particulate composite in the Al_2O_3-ZrO_2-WC carbide system shows promising properties in structural applications especially as wear resistant parts. Mentioned materials show the unique microstructure of sintered bodies composed of three continuous polycrystalline subsystems mutually penetrating each other. Despite of mechanical properties of constituent phases, its properties depends on the residual stress state and the microstructure. Especially important is the interphase grain boundaries state. Significant differences of thermal properties of constituent phases create during composite manufacturing meaningful residual stresses (locally exceeded 1.5 MPa). It can influence the interphase boundaries structure. The Paper presents results of investigation of high-resolution transmission electron microscopy (HREM) on the different type grain boundaries structure and its chemical composition.

Keywords: composites, microstructure, zirconia, alumina, tungsten carbide

1 Introduction

Sintered composites with alumina or/and zirconia matrix were identified as relatively low cost materials showing very good abrasive wear resistance [1, 2]. Fabrication of the dense composite materials using typical powder compacting technology and following sintering process meets many barriers connected with each step of this technology. Application of submicro- or nanosized powders increases difficulties occurring during manufacturing [3 ,4].
The first task for applied technology is to assure the uniformity of different phase distribution in prepared composite powder. The process must eliminate the possibility of one phase grains aggregation. If it is performed with success, sintering could provide to homogeneous composite body with properties significantly improved in relation to pure matrix material [5–7].
Usually it is profitable for sintering process to avoid of chemical reactions, nevertheless sintering must be provided at temperatures, which assure the effective mass transport in sintered phases.
Additionaly, after sintering process, during cooling, in dense multiphase bodies residual stresses could be created due to thermal expansion coefficient mismatch [8, 9].
This work shows the results of detail investigation of the fine-grained microstructure of three-phase composite containing comparable amount of each phase. The special care was put to

describe grain boundaries between the grains of different phases (i. e. alumina-carbide or zirconia-carbide) because the state of interphase boundaries strongly influenced the composite properties [10-12].

2 Experimental

Al_2O_3-ZrO_2-WC composite powder was prepared from commercial powders (α-alumina: TM-DAR, Taimei Chemicals; yttria stabilized zirconia: 3Y-TZ, Tosoh and tungsten carbide: Baildonit) by wet (ethanol) mixing in attritor. The volume proportion of each phase was 1:1:1. Sintering of composite bodies was conducted in the Thermal Technology hot-press device at 1650ºC (with 45 min. soaking time) in argon atmosphere under 25 MPa pressure. Density of sintered bodies was 8.46 g/cm^3 (98.5% of theoretical value).

The structure investigations were performed in Tecnai G2 FEG microscope dedicated for high resolution (HREM) observations. The thin foils were prepared by cutting thin slices of compacts using diamond sow and followed dimpling and ion milling using Gatan equipments. Finally the samples were covered by carbon thin layer in order to assure their conductivity.

The chemical analyses both point and line scans were performed in the HAADF/STEM mode using a energy dispersive X-ray spectrometry (EDS).

3 Results

Fig. 1 presents a set of high angel angular dark field (HAADF) image and corresponding elemental mapping images recorded in the STEM mode on a marked area.

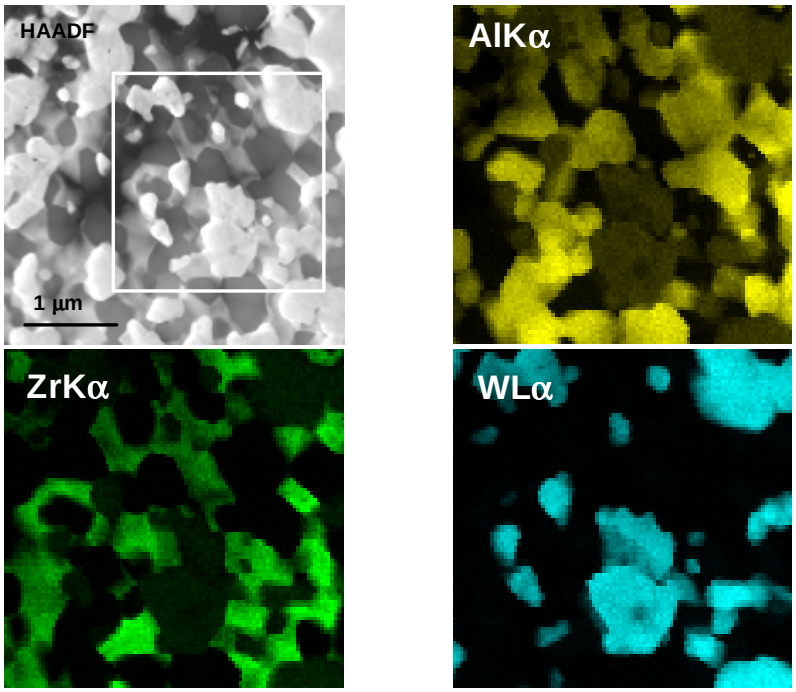
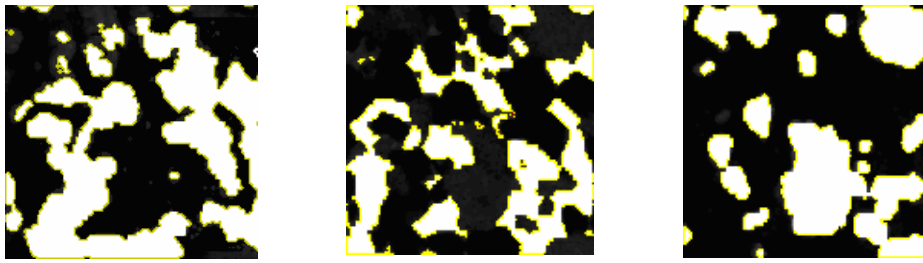


Fig.1 HAADF image and corresponding elemental mapping images recorded along marked area.

The obtained contrast is due to a different atomic number of elements (Z^2-contrast) and it allows to analyze a particulate phases. Taking to the account a distribution of Al, Zr and W, we can

calculate the mean grain size of Al_2O_3, ZrO_2, WC phases, respectively. In this purpose the image analyze software Gatan Digital Micrograph ™ 3.10.0 was used. The procedure of analyze was as follow: the elemental mapping images of Al, Zr and W were filtered applying "*maximum*" filter, then from obtained binary images the histograms of gray level were created and determination the threshold for maximum intensity of particulate phases were performed. Finally, we obtained the images of particulate phases and measured values of their mean grain size and filled area (**Fig. 2**). The mean grain sizes of investigated phases were as follow: Al_2O_3 – 330 nm, ZrO_2 – 280 nm and WC – 340 nm, and relative area friction: 35.8, 30.7, and 33.5%, respectively. The obtained data were in a good agreement with these used as initial conditions for preparing of compacts (size of powders and volume proportion of each phase). Calculated mean grain size values for composite components are comparable with these calculated using much smaller image magnifications presented in [13].



Al_2O_3 - 35,8% ***ZrO_2 - 30,7%*** ***WC - 33,5%***

Fig.2 Results of images analyze showing distribution of particulate phases in the area indicated in Figure 1.

In order to analyze the grain boundaries between particulate phases a line scan analyses were performed for several grains. **Fig. 3** presents result of line scan analyse between WC and Al_2O_3 grains performed along the marked line.

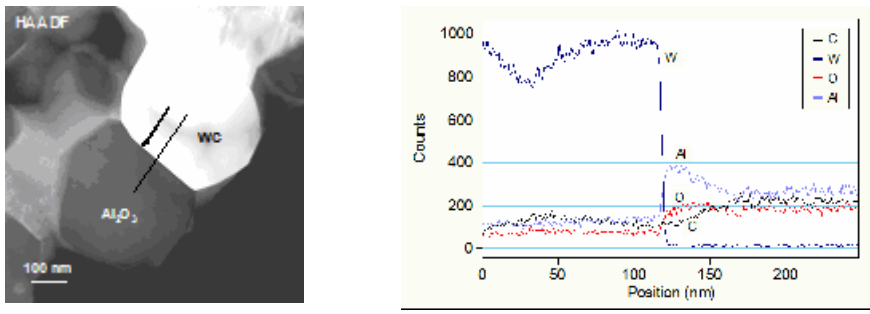


Fig.3 HAADF image of composite microstructure and result of line scan analyze across the WC and Al_2O_3 grains boundary.

One can see that both Al and W concentration is changing very sharp close the boundary, it means that no diffusion of this elements occurs. Concerning concentration changes of O, and C, is difficult to say about their diffusion, due to contamination effect, limit of detection of light elements by EDS method, thickness of sample and finally necessity of covering by the carbon nonconductive ceramic sample. Additionally, there is no information about the thickness of grains, therefore the overlapping of signal from different grains can occurs.

The observations of grain boundaries were performed in atomic scale also. **Fig. 4** presents the high-resolution transmission electron microscopy (HRTEM) showing grains boundary between WC and Al_2O_3.

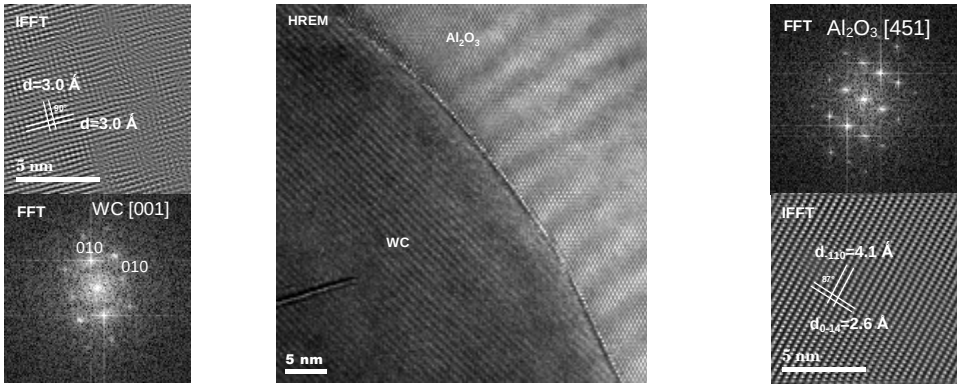


Fig.4 HRTEM image and corresponding FFT and IFTT images showing the grains boundary between WC and Al_2O_3.

One can see the sharp boundary between [001] and [451] oriented grains of WC and Al_2O_3 phases, respectively. The inverse fast Fourier transform (IFFT) images showed that Al_2O_3 is almost free from structural defects, whereas plenty of dislocations and stacking faults on {010} planes can be distinguish in WC grain.
Fig. 5 presents a result of line scan analyse between WC and ZrO_2 grains performed along the marked line.

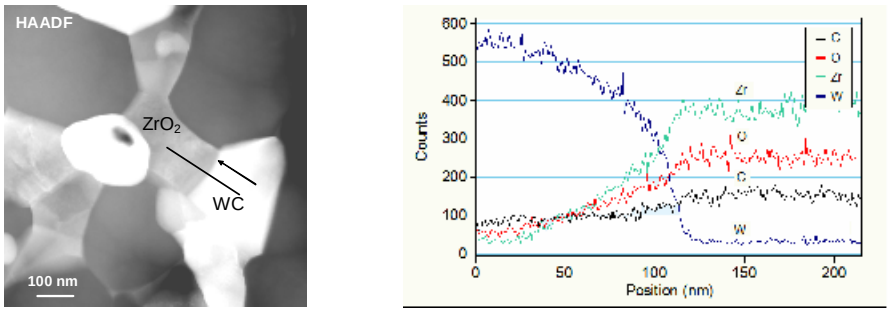


Fig.5 HAADF image of composite microstructure and result of line scan analyze across the WC and ZrO_2 grains boundary.

One can see that signal originating from Zr increases in measurement range form 25 nm up to about 110 nm reaching maximum inside the ZrO_2 grain. This behaviour can be explain as both overlapping of the WC and ZrO_2 grains or some diffusion of Zr into WC grain. However taking to the account character of signal originating form O (almost the same as in case of Zr) most probably this first one explanation is correct. The above assumption that the grain boundaries in Al_2O_3-ZrO_2-WC composite are free from additional phases was proofed by high resolution observation.

Despite of chemical reaction, during high temperature treatment, some chemical elements segregation could occurs. In the WC grain the W/C and W/O ratio was changing continuously. It suggests that during sintering oxygen diffuse into the carbide structure. Parallel, carbon changes its content in carbide grain what has to change locally WC stoichiometry. It was previously observed in [14].

Fig. 6 presents HRETM image showing a triple point between three phases. Each type of interphase boundaries is represented Al_2O_3-ZrO_2, Al_2O_3-WC and ZrO_2-WC. The corresponding fast Fourier transforms (FFT) allowed to identify the crystallographic structure of coexistence phases. The tetragonal ZrO_2 with [111] orientation, $L1_2$ WC with [001] orientation and hexagonal Al_2O_3 with [451] orientation were identified respectively by measurement of distances and angles on corresponded FFT's images. The phase boundaries areas did not show additional phases inside.

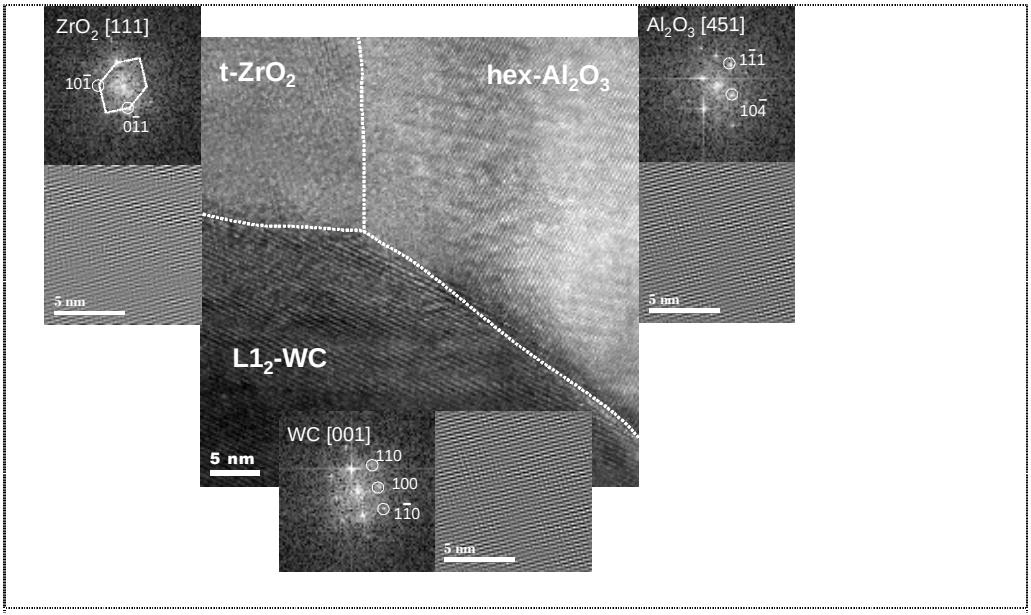


Fig.6 HRETM image showing a triple point between three phases, corresponding FFT and IFFT images

4 Conclusions

Investigations showed that the composite microstructure consisted of sub-micrometric grains of each phase randomly and homogeneously distributed. The grains boundaries were distinct and clear. This confirms high purity of used starting powders and a lack of chemical reactions between constituent phases at applied sintering conditions. HREM observations of interphase boundaries and the corresponding fast Fourier transforms (FFT) and inverse fast Fourier transforms (IFFT) allowed to identify the crystallographic structure of coexistence phases in boundaries area.

Local changing of the chemical composition of WC phase in contact with zirconia grains was detected. However, its nature should be elaborate in details, distinct changes of O/W and C/W ratios suggest that in the area of WC/zirconia interphase boundary chemical changes occurred.

WC in contact with alumina was stable. There were no distinct chemical changes on the WC/alumina interphase boundary.

Acknowledgements

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References

[1] Z. Pędzich: The Abrasive Wear of Alumina Matrix Particulate Composites at Different Environments of Work: In: Advanced Materials and Processing IV, D.Zhang, K.Pickering, B. Gabbitas, P. Cao, A. Langdon, R. Torrens,J. Verbeek (Eds.), Trans Tech Publications, Switzerland, 2007, p. 283-286.
[2] D. Galusek et al.: Journal of the European Ceramic Society, Vol. 27, 2007, No. 2–3, p. 1237-1245.
[3] M. N. Rahaman: Ceramic Processing, Univ. Michigan, 2006.
[4] R. Rice: Processing of Ceramic Composites, In: Advanced Ceramic Processing and Technology, vol. 1, J.G.P. Binner (Ed.), Noyes Publications, 1990.
[5] K. Niihara: Journal of the Ceramic Society of Japan, Vol. 99, 1991, No. 10, p. 974-982.
[6] L. Gao et al.: Journal of the European Ceramic Society, Vol. 19, 1999, p. 609-613.
[7] Z. Pędzich, K. Haberko, J. Piekarczyk, M. Faryna, L. Lityńska: Materials Letters, Vol. 36, 1998, p. 70-75.
[8] G. Grabowski, Z. Pędzich: Journal of the European Ceramics Society, Vol. 27, 2007, No. 2-3, p. 1287-1292.
[9] G. Grabowski, L. Stobierski, P. Rutkowski: Internal sources of damage in ceramic materials, In Realiability of Ceramics, K Haberko, M .M. Bućko (Eds.): Ceramika/Ceramics, Vol. 97, 2006 p. 293-298.
[10] Z. Pędzich, K. Haberko, M. Faryna, K. Sztwiertnia: Key Engineering Materials, Vol. 223, 2002, p. 221-226.
[11] Z.Pędzich, M.Faryna: Key Engineering Materials, Vol. 290, 2005, p. 142-148.
[12] K. Sztwiertnia, M.Faryna, G. Sawina: Journal of the European Ceramics Society, Vol. 26, 2006, p. 2973-2978.
[13] Z. Pędzich: Materiały Ceramiczne, Vol. 61, 2009, No. 2, p. 15 (in Polish).
[14] K. Haberko, Z. Pędzich, J. Piekarczyk, M.M. Bućko, W. Suchanek: Tetragonal Zirconia Polycrystals Under Reducing Conditions, In: Third Euro-Ceramics, vol. 1, P. Duran, J.F. Fernandez (Eds.), Faenza Editrice Iberica S.L., Spain, 1993, p. 967.