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MICROBEAM STUDIES OF ALUMINA-BASED COMPOSITE

BADANIA MIKROSTRUKTURALNE KOMPOZYTU NA OSNOWIE Al_2O_3

Application of alumina as a composite matrix with tungsten carbide as a reinforcing additive leads to a new class of structural ceramics of improved mechanical properties. To explain enhanced mechanical properties of the system two microanalytical methods i.e.: transmission electron microscopy (TEM) and electron backscatter diffraction (EBSD) in the scanning electron microscope (SEM) were applied. Automatic orientation measurements in the SEM is preferable to the TEM for microstructure characterisation, because no sample thinning is required, reflector data needed for EBSD indexing are easily available and the analysed area could be greatly increased. Alumina-based composite with 10 vol. % tungsten carbide (WC) was chosen for EBSD measurements since preliminary TEM work has already shown specific crystallographic relationships between matrix and carbide phases. Such correlations may partially explain significant improvement of mechanical properties of alumina-based composite comparing with a pure Al_2O_3 matrix. However, apart from crystallographic factors, the properties of material under investigation may be affected by interfacial defects and interphase boundary structure. Thus, high-resolution electron microscopy investigations were required to complete information about composite behaviour and control its properties.

Keywords: Alumina-based composite, Al_2O_3/WC composite, transmission electron microscopy (TEM), electron backscattered diffraction (EBSD)

Zastosowanie tlenku aluminium (Al_2O_3) jako matrycy kompozytów ceramicznych wzmacnianych fazą węglikową prowadzi do wytworzenia nowej klasy ceramiki strukturalnej o podwyższonych właściwościach mechanicznych w porównaniu z czystą matrycą. Aby wyjaśnić przyczynę znaczącego wzrostu tych właściwości, zastosowano dwie techniki mikroanalityczne, a mianowicie transmisyjną mikroskopię elektronową (TEM) oraz dyfrakcję elektronów wstecznie rozproszonych w skaningowym mikroskopie elektronowym (EBSD/SEM). Zautomatyzowane pomiary orientacji w SEM posiadają istotną przewagę nad pomiarami orientacji w TEM ze względu na szereg czynników takich jak: wyeliminowanie czasochłonnego przygotowywania cienkich folii, dostępność bazy danych krystalograficznych potrzebnych do utworzenia wzorców do pomiarów EBSD a także zwielokrotnienie objętości analizowanego kompozytu. W niniejszej pracy przebadano pod względem mikrostrukturalnym kompozyt na bazie Al_2O_3 z 10% udziałem objętościowym wzmacniającej fazy węglikowej (WC). Kompozyt ten wybrano ze względu na fakt występowania pewnych, specyficznych zależności krystalograficznych pomiędzy krystalitami osnowy i węglika wolframu, co stwierdzono za pomocą dyfrakcji SAED w TEM. Takie zależności, występujące w całej objętości badanego materiału, mogą wyjaśniać poprawę właściwości mechanicznych kompozytu w porównaniu z czystą matrycą. Na właściwości te ma również wpływ struktura granic międzyfazowych a także obecność fazy amorficznej. Dlatego też w pracy przedstawiono jakościową analizę takich granic wykonaną za pomocą wysokorozdzielczego transmisyjnego mikroskopu elektronowego (HREM).

1. Introduction

The microstructure of ceramic composites can be better understood by establishing crystallographic relationships both between several adjacent crystallites and between the matrix and reinforcing additives. Such a determination was successfully performed using SAED obtained with TEM. Thin foil examination revealed also information about the presence of cracks and voids.

However, during TEM observations the investigated area is usually limited to only few crystallites. Thus, it is difficult to collect reasonable amount of statistical data. Also preparation of thin foils from ceramic composites including phases of different hardness is tedious and time-consuming. To overcome such problems the

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technique of Orientation Mapping (OM) using Electron BackScatter Diffraction in the Scanning Electron Microscope (EBSD/SEM) has been employed [1-3]. It provides information about orientations of crystals with spatial resolution in the range of a few tenths (in a case of FEG SEM) to hundreds of nanometers, depending on the beam accelerating voltage, specimen tilt and probe size as well as specimen density. Recent development in data processing has also improved significantly angular resolution up to 0.5°. By applying the EBSD technique a relatively large number of diffraction patterns from several hundreds of neighbouring crystallites can be collected, indexed and stored during one single experiment. Consequently, orientation relationships between several or even hundreds of crystallites can be established giving a sufficient ground for general characteristics of the material under investigation.

The aim of the paper is to establish the crystallographic relationships between the Al_2O_3 matrix and reinforcing WC additive in thin foils and in a larger volume. An attempt will be made to explain a significant improvement of mechanical properties of alumina-based composite over the Al_2O_3 polycrystalline compacts.

2. Experimental

Alumina-based composite reinforced with 10 vol. % of tungsten carbide hot pressed at 1700°C for 4 h was analysed by the TEM, SEM and EBSD techniques. A Philips CM 20 (200 kV) equipped with an LaB_6 gun and double tilt analytical holder and Si (Li) drifted detector and EDAX Phoenix energy dispersive (EDS) X-ray analyser was used for TEM experiments. The specimen suitable for such observations was prepared by cutting 3 mm diameter disc and polishing it to a thickness of 30 to 40 μm. Then it was dimpled in a GATAN Dimple grinder up a thickness of less than 10 μm and finally thinned by ion milling by use of a GATAN Duo Mill.

The SEM and EBSD measurements were carried out in a LEO 1438 VP scanning electron microscope with hairpin tungsten gun at the acceleration voltage 20 kV, tilt angle 70° and working distance 25 mm in a variable pressure mode to neutralize a negative charge gathered on the surface of ceramic composite. The variable pressure in the SEM chamber was preferred over the carbon coating due to the fact that the latter deteriorate the Kikuchi bands quality and significant decrease the number of solved patterns [4]. The backscatter diffractions were automatically acquired and indexed by the TSL TexSEM hardware at the Max-Planck-Institut für Metallforschung in Stuttgart. Then, detailed data analyses were performed at the Institute of Metallurgy and Materials Science in Krakow. Two HKL Technology CHANNEL 5 software programmes, mainly *Tango* for generating a wide variety of maps (including orientation and phase maps) and *Mambo* for producing pole figures and inverse pole figure from EBSD orientation data, were applied. The 0.25 μm and 0.2 μm steps between EBSD analytical points (grid resolutions) to reveal fine microstructure details were used.

To perform electron backscatter diffraction analysis two different match units for Al_2O_3 and WC, containing reference crystal data and lists of Kikuchi bands for each of these phases, were created. For this purpose, precise diffraction data recorded by the X-ray diffraction (XRD) had to be evaluated. The following values were used for match unit creation: the trigonal form of Al_2O_3 shows the D_3 symmetry with lattice parameters a = 4.758 Å and c = 12.991 Å; the hexagonal form of WC shows D_6 symmetry with lattice parameters: a = 2.9046 Å and c = 2.8356 Å. No difficulties with misindexing and/or pseudo-symmetry were met and both EBSD systems, i.e. the TSL and HKL had no problems with distinguishing Al_2O_3 and WC phases.

The EBSD signal is generated in the outermost layers of the sample (of a few tens of nanometers). Thus, the samples were carefully prepared to eliminate any surface damage. Conductive thermoplastic resin was used for mounting. Then, the sample was polished with diamond pastes of decreasing grain size and, finally, by colloidal silica under decreasing pressure (30-5 N).

The EBSD measurements require the size of crystallites above the resolution of the method. For typical resolution of 200 nm (or better) obtained in the SEM with W filament, the crystallite size should be above 1 μm to get reasonably good statistics.

3. Results and discussion

Establishing the crystallographic relationships between adjacent crystallites of Al_2O_3 and WC provides insight into the nature of toughening. Observations performed with the TEM indicated high density of investigated composite. However, in some triple points fairly large pockets of glassy phase were observed (Figs. 1 and 2). Several alumina and WC crystallites were indexed using the SAED and two dominating crystallographic relationships between above phases were identified (Figs 2 and 3):

$$(0\bar{1}11)WC \parallel (1\bar{1}05)Al_2O_3$$

$$[11\bar{2}3]WC \parallel [\bar{2}3\bar{1}1]Al_2O_3$$

and

$$(0\bar{1}11)WC \parallel (\bar{1}011)Al_2O_3$$

$$[2\bar{1}\bar{1}0]WC \parallel [01\bar{1}1]Al_2O_3.$$

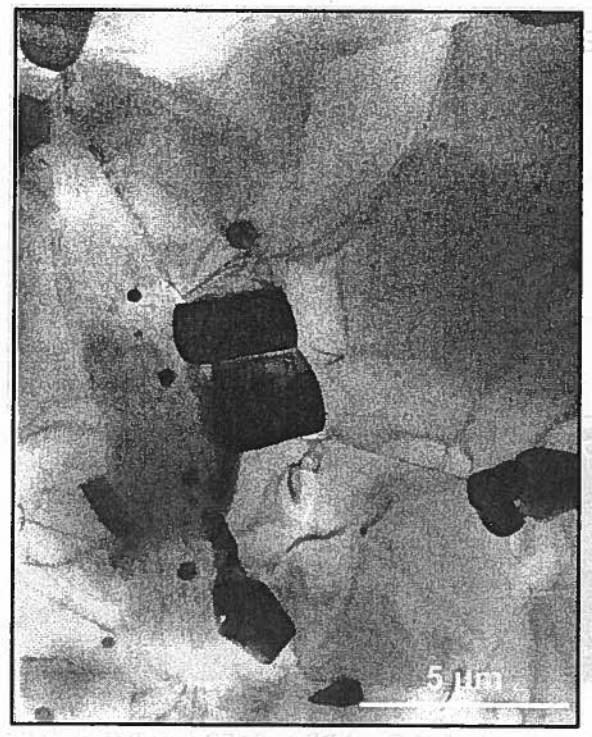

Fig. 1. TEM micrograph of Al_2O_3 / WC system

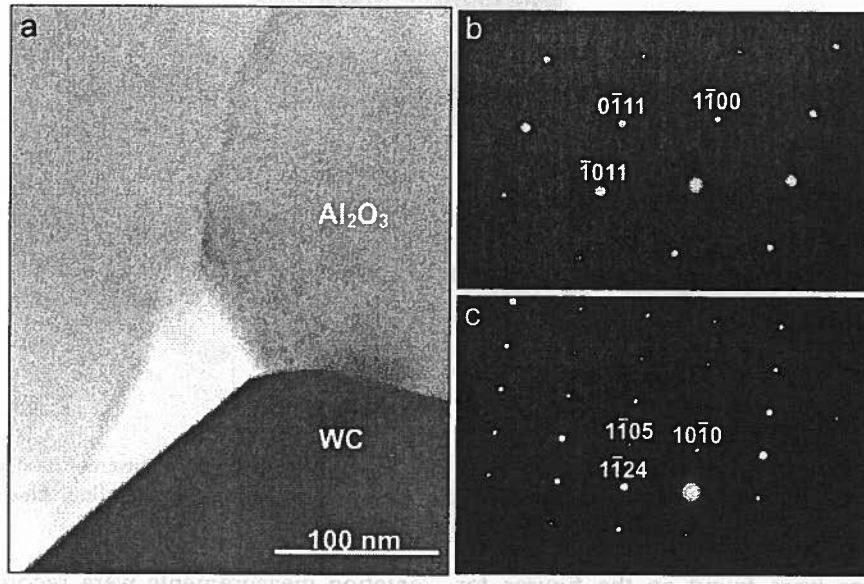

Fig. 2. TEM micrograph of Al_2O_3, a) BF, b) SAED from WC, c) SAED from Al_2O_3

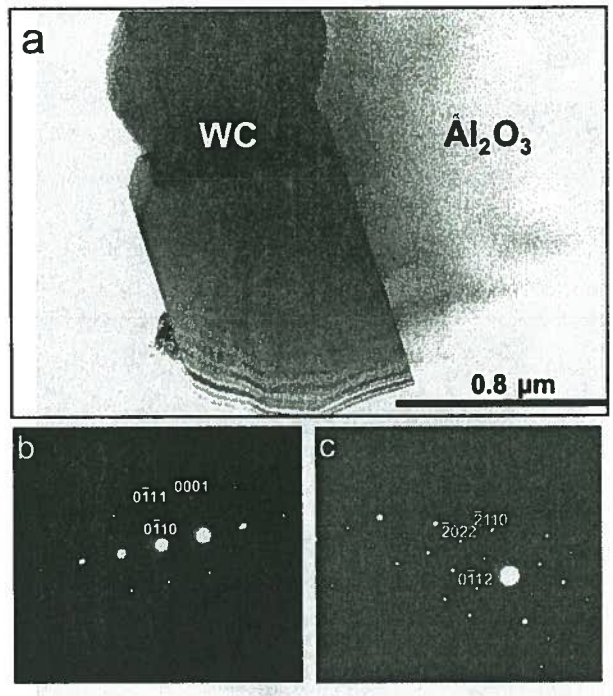

Fig. 3. TEM micrograph of Al_2O_3, a) BF, b) SAED from WC, c) SAED from Al_2O_3

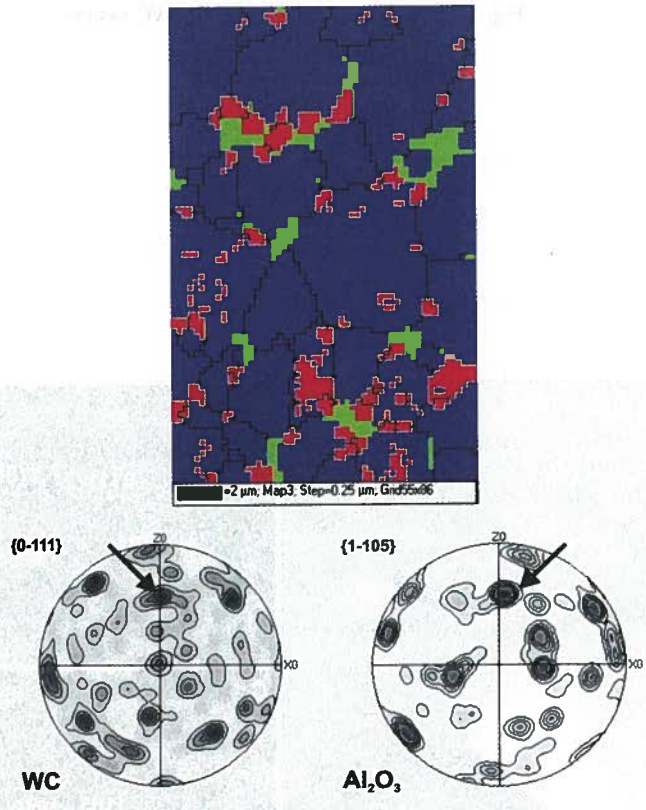

Fig. 4. EBSD phase map. Blue and red regions represent Al_2O_3 and WC, respectively; green areas have not produced analysable diffraction pattern. High-angle grain boundaries (>15°) were also displayed. Pole figures (planes) represent crystallographic relationship from Fig. 2. Arrows show the same pole present on the Figures for both composite components

These relationships were found on the figures for several sites investigated on the thin foil. To verify the above correlations in a much larger volume single orientation measurements were recorded and displayed in a form of phase orientation maps (Figs 4 and 5).

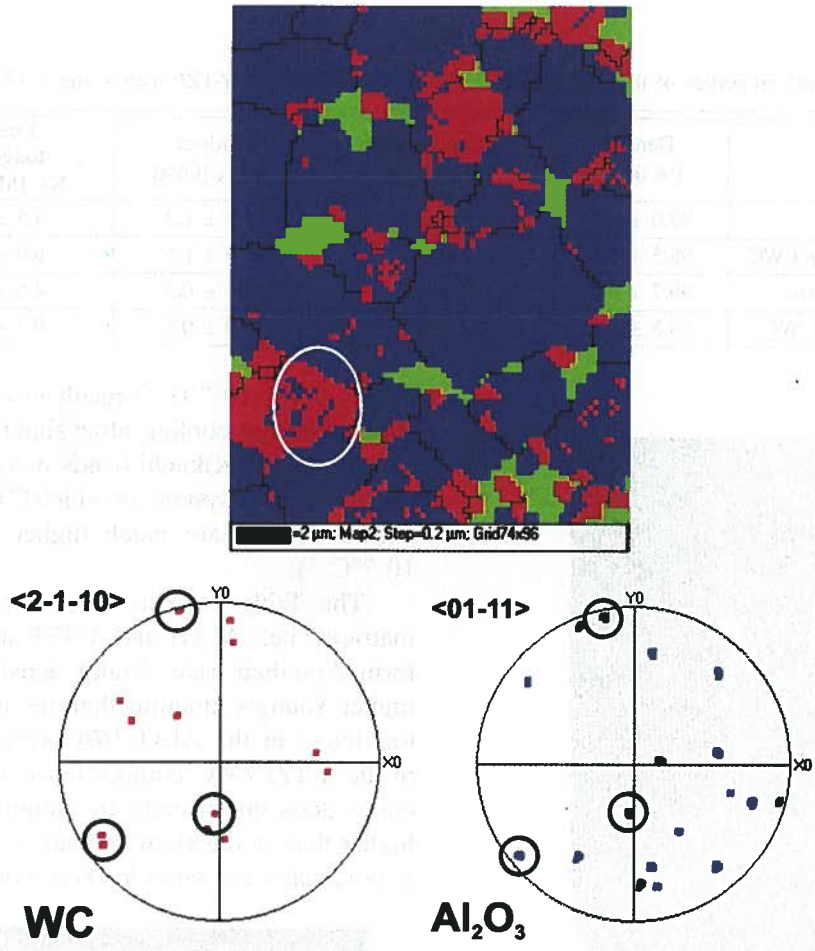

Fig. 5. EBSD phase map. Blue and red regions represent Al_2O_3 and WC, respectively; green areas have not produced analysable diffraction pattern. High-angle grain boundaries (>15°) were also displayed. A marked subset (white circle) displays the region from which pole figures (directions) representing crystallographic relationship shown in Fig. 3 were calculated

Stereographic projections of particular crystal directions in the alumina and tungsten carbide phases were calculated from the fraction of a data set called "subset". It was selected from orientation map in order to analyse the orientation properties of small-scale areas where crystallites of both phases exist. Figs 4 and 5 show two typical examples (chosen from dozen already measured) of the crystal directions arrangements in the neighbouring crystallites of Al_2O_3 and WC phases. It can be seen that in the adjacent alumina and tungsten carbide crystallites certain planes, mainly: $(1\ \bar{1}\ 05)$ in Al_2O_3 and $(01\ \bar{1}\ 1)$ in WC as well as directions $<01\ \bar{1}\ 1>$ in Al_2O_3 and $<2\ \bar{1}\bar{1}\ 0>$ in WC are nearly parallel. These results confirm previous SAED measurements performed using TEM, however on a much larger scale.

High resolution electron microscopy (HREM) observations showed that most crystallites of both composite phases have a direct contact (Fig. 6). However, in some places the presence of thinner or thicker layers of amorphous materials resulting from sintering additives was also noted (Fig. 7). It is significant that in the cases where good match between crystal lattices was established, the amorphous layer even on the same crystallite face thinned significantly (Fig. 8).

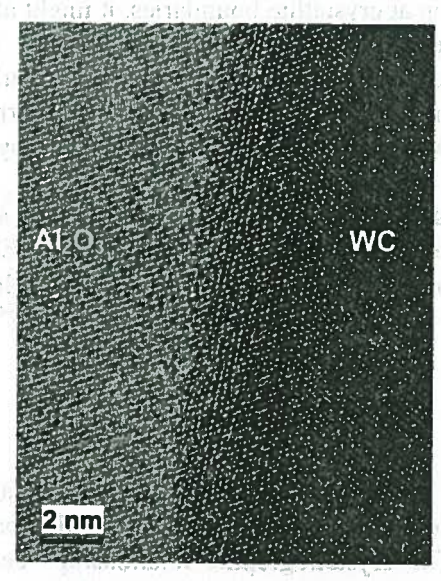

Fig. 6. A HRTEM image of planar phase boundary separating Al_2O_3 and WC

TABLE

Comparison of mechanical properties of the Al_2O_3 matrix, Al_2O_3 / WC composite, Y-TZP matrix and Y-TZP / WC composite

Material	Density [% theo.]	Young modulus E [GPa]	Hardness $HV_{0.5}$ [GPa]	Fracture toughness K_{Ic} [$MPam^{0.5}$]
Al_2O_3	99.0 ± 0.1	380 ± 5	15.0 ± 1.2	4.5 ± 0.5
Al_2O_3 + 10% vol.WC	98.5 ± 0.1	430 ± 3	17.0 ± 1.5	6.0 ± 0.6
Y-TZP matrix	99.7 ± 0.1	209 ± 3	14.1 ± 0.3	4.6 ± 0.5
Y-TZP + 10% WC	98.8 ± 0.1	232 ± 2	19.0 ± 0.6	9.7 ± 1.0

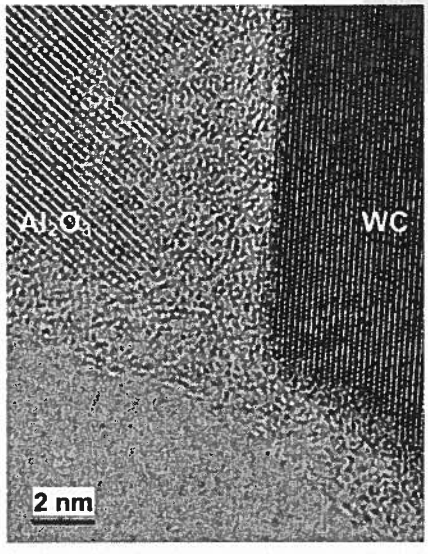

Fig. 7. A HRTEM image of planar phase boundary separating Al_2O_3 and WC with a layer of amorphous phase along the interface

Even as an overall amount of the amorphous material in the present Al_2O_3 / WC composite was small due to its location at crystallite boundaries, it might affect composite mechanical properties quite strongly. Therefore, the further optimization of this material should include the description of the distribution of the amorphous material as well as suggestions how to control it by changing sintering conditions.

It must be added that in the investigated system the thermal expansion coefficient mismatch (CTE) is not as large as in the other composites [7]. The values of the CTE for Al_2O_3 and WC ($\alpha_{Al_2O_3} = 7 \times 10^{-6}°C^{-1}$ and $\alpha_{WC} = 5.2 \times 10^{-6}°C^{-1}$) result in relatively low internal stresses during cooling after sintering. This fact results also in sharper Kikuchi bands images as compared with the Y-TZP /WC system, in which CTE mismatch-induced tensile stresses are much higher ($\alpha_{Y\text{-}TZP matrix} = 11 \times 10^{-6}°C^{-1}$).

The Table presents mechanical properties of two matrices, i.e.: Al_2O_3 and Y-TZP as well as composites formed on their basis. Highly densified composites show higher Young's modulus than the matrices. The fracture toughness in the Al_2O_3 / WC system is not as high as in the Y-TZP / WC composite (as transformation toughening does not operate in alumina), though it is still higher than in the alumina matrix. The Vickers hardness is practically the same for both composite systems.

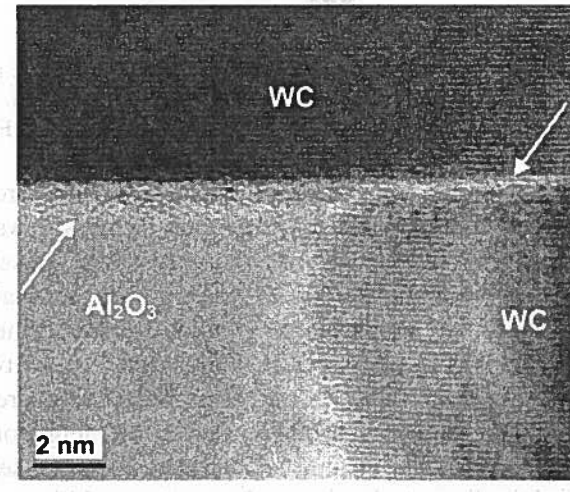

Fig. 8. A HRTEM image of planar phase boundary separating Al_2O_3 and WC. Differences in thickness of amorphous layer is shown

4. Summary

The TEM observations and EBSD measurements were successfully used to analyse alumina-based composite. The crystallographic relationships between the Al_2O_3 matrix and reinforcing WC additive were established both locally and in statistically significant composite sections.

The presence of crystallographic correlations between matrix and reinforced carbide may, at least partially, explain significant improvement of mechanical properties of alumina-based composite over the Al_2O_3 polycrystalline compacts. The performed observations proved also the presence of small amount of amorphous phase at some crystallite faces resulting from sintering additives. The further optimization of Al_2O_3 / WC composite

should both explain the effect of distribution of amorphous materials on mechanical properties and investigate possibilities how to control it.

Finally, alumina-based composites may replace the expensive TZP-based composite in diverse applications where enhanced hardness, toughness and wear resistance is required, e.g.: for lining for pipes and vessels, pump and faucet seals, thread and wire guides.

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