INSTITUTE OF HIGH CURRENT ELECTRONICS SB RAS

NATIONAL RESEARCH TOMSK POLYTECHNIC UNIVERSITY

ZIRCONIA-BASED COMPOSITES REINFORCED BY CARBON NANOMATERIALS

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Topicality

3 mol % yttria-stabilized zirconia (3YSZ or ZrO_2) has being used as a structural material for applications such as thermal barrier coatings (TBCs) in gas-turbine engines, pistons, plungers, blade cutting tools, abrasion resistant components, precision measuring gauges, and ceramic ball valves because of its high hardness, excellent chemical inertness, wear resistance and low thermal conductivity. Recently, 3YSZ has also being used as bio-structural material for applications including dental crowns, hip and knee prostheses, temporary supports, and tibial plates due to of its biocompatibility, low cytotoxicity and reduction of bacterial adhesion with low corrosion potential. However, ceramics brittleness restricts them from diverse structural applications and it has been a continuous driving force to encourage researchers to use new approaches with the aim of toughening ceramics.

The main strategies for improving the mechanical properties of ceramics are nanostructuring of grains and the addition of reinforcements. In recent years, the emergence of graphene, a monolayer of sp^2-hybridized carbon atoms arranged in a honeycomb lattice, has attracted increasing interest due to its impressive properties such as high Young modulus (≈ 1.0 TPa), a fracture strength of 130 GPa that open a wide number of opportunities for the manufacture of ceramic matrix composites. However, carbon nanotubes are also widely used as a reinforcing additive, as they have unique properties. For example, Young’s modulus can reach 1470 GPa in single-walled carbon nanotubes and 950 GPa in multi-walled carbon nanotubes (Young’s modulus of diamond is about 1.2 TPa).

Purpose of research

The purpose investigate the effect of additives SWCNTs, MWCNTs and GNPs on the microstructure, phase composition, densification, microhardness, fracture toughness and crack propagation of ceramic composites with a ZrO_2 matrix.

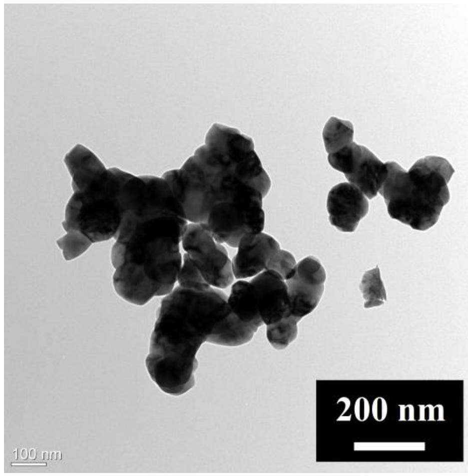
Single-walled carbon nanotubes – SWCNT,

Multi-walled carbon nanotubes – MWCNT;

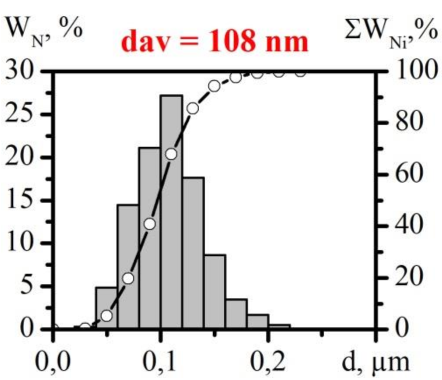
Graphene nanoplatelets – GNP.

The starting materials

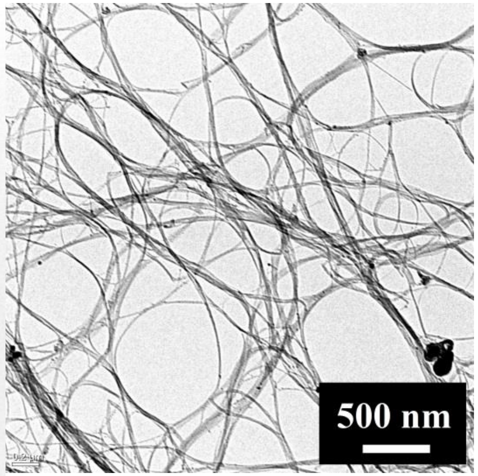
ZrO_2 with 3 mol.% Y_2O_3 (TZ-3YS), Tosoh, Japan



S_{BET} = 5,66 m^2/g.



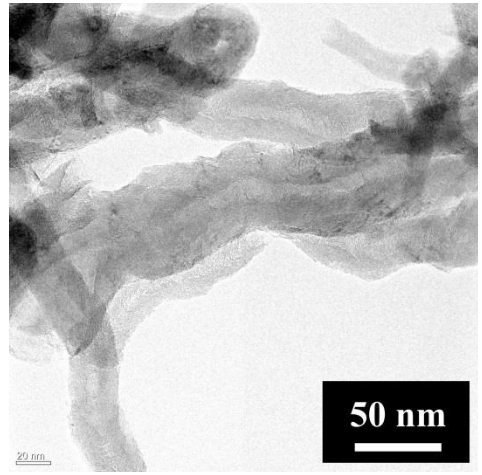
SWCNTs (Tuball), OCSiAl, Russia



S_{BET} = 546 m^2/g.

Manufacturer data for SWCNT-products TUBALL	
Diameter	1-3 nm
Length	>5 µm
SWCNTs content	~ 75 wt.%
Non-carbon impurities	< 17 %

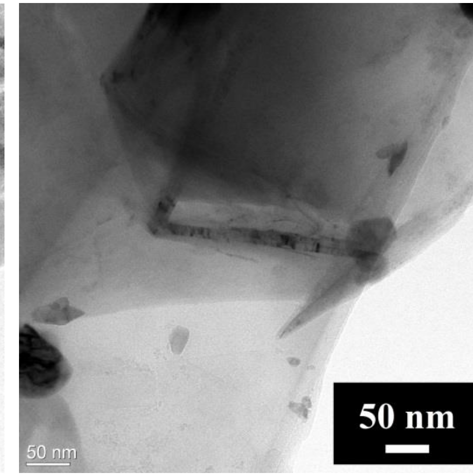
MWCNTs (Taynit), NanoTechCenter, Russia



S_{BET} = 103 m^2/g.

Manufacturer data for MWCNT-products TAYNIT	
Diameter	20-50 nm
Length	≥2 µm
MWCNTs content	~ 93 wt.%
Non-carbon impurities	≤10 wt.%

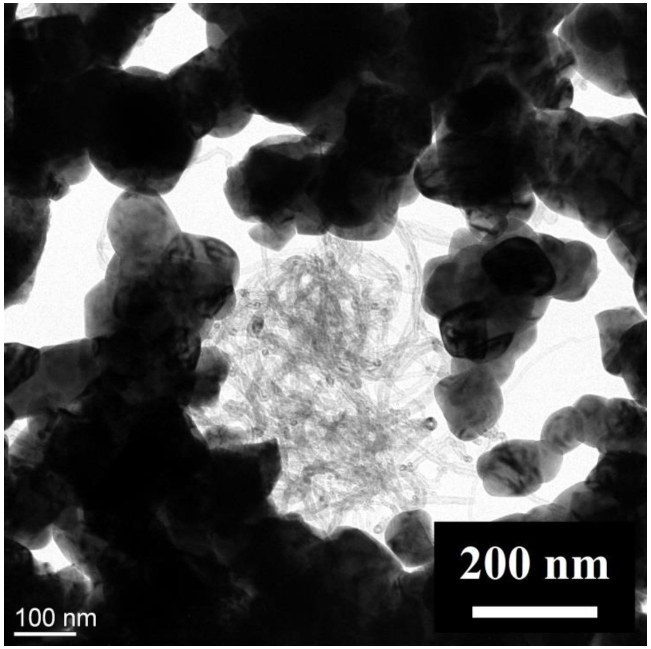
GNPs, NanoTechCenter, Russia



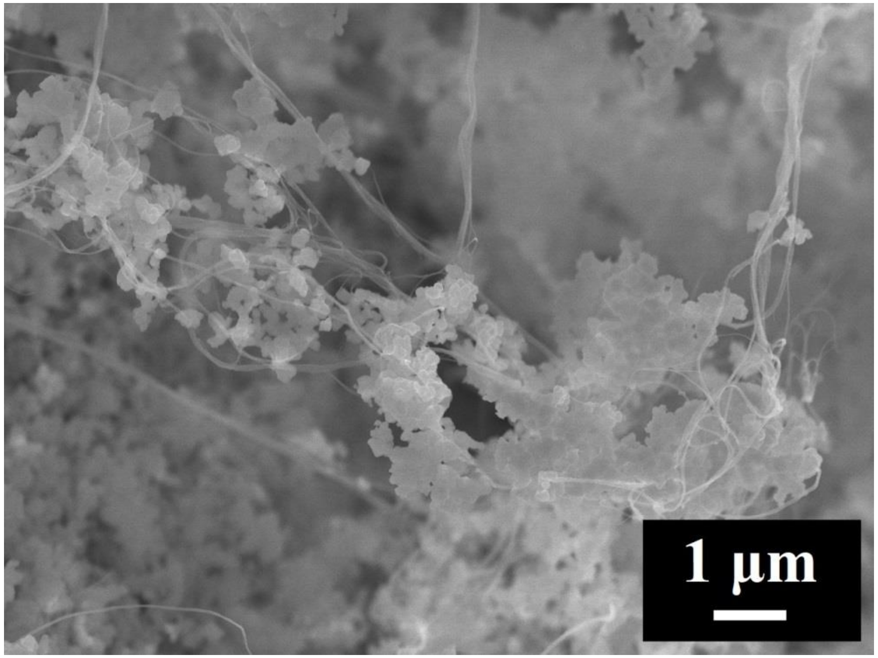
S_{BET} = 25 m^2/g.

Manufacturer data for GNP-products	
Layers	~ 15-25
Thickness of the nanoplates	6-8 nm
Size	2-10 µm

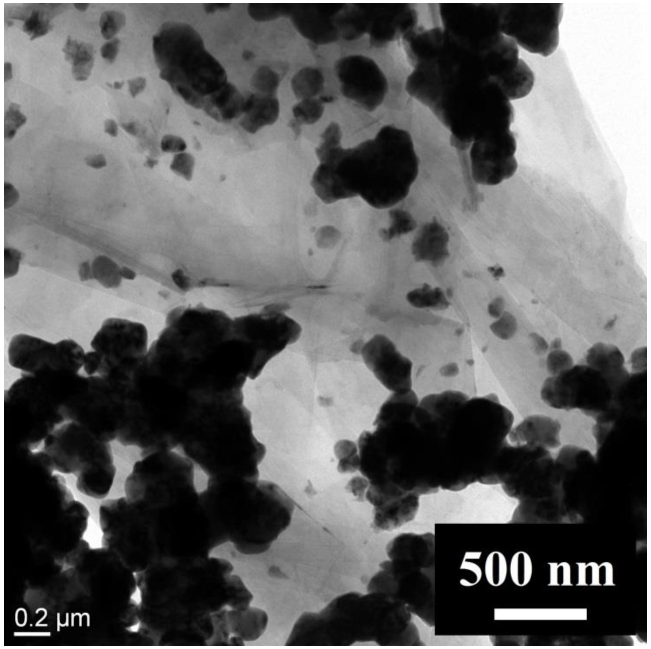
Prepared composite powders



ZrO_2
+ 1wt.%
MWCNT



ZrO_2 + 1wt.% SWCNT



ZrO_2
+ 1wt.%
GNP

Materials and methods

SPS-515S, Syntex Inc., Japan

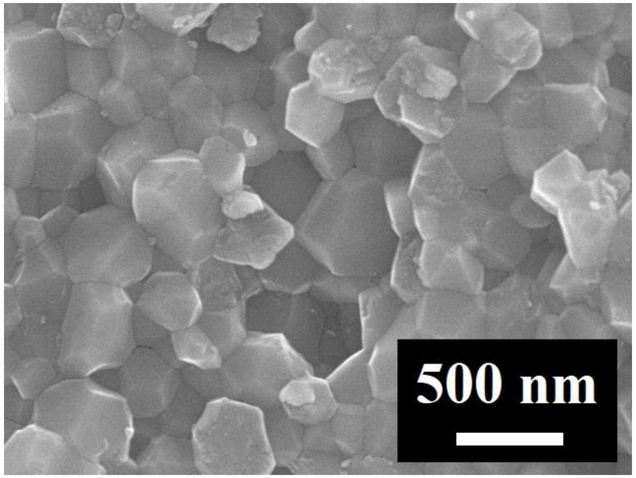
Spark plasma sintering:

- sintering temperature – 1500 °C;
- heating rate – 100 °C/min;
- holding time – 10 min;
- uniaxial mechanical pressure – 40 MPa.

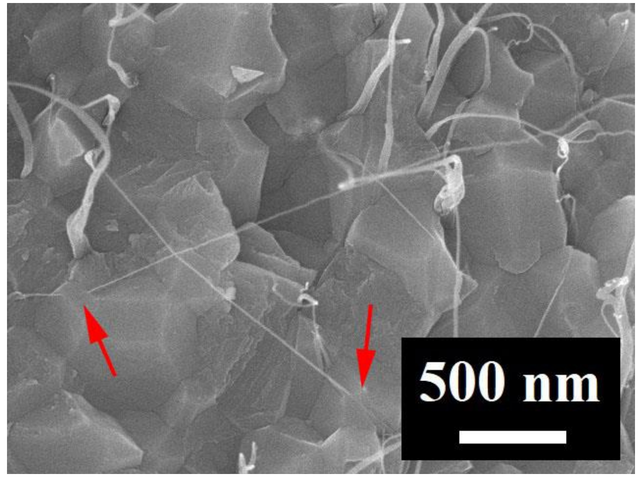
The following samples were sintered:

Sample
ZrO_2 without additives
ZrO_2 + 1wt.% SWCNT
ZrO_2 + 1wt.% MWCNT
ZrO_2 + 1wt.% GNP

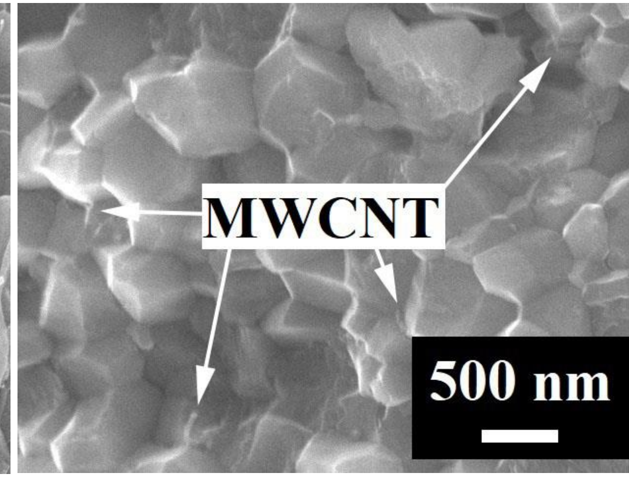
The microstructure of composites based on ZrO_2 with different carbon nanomaterials



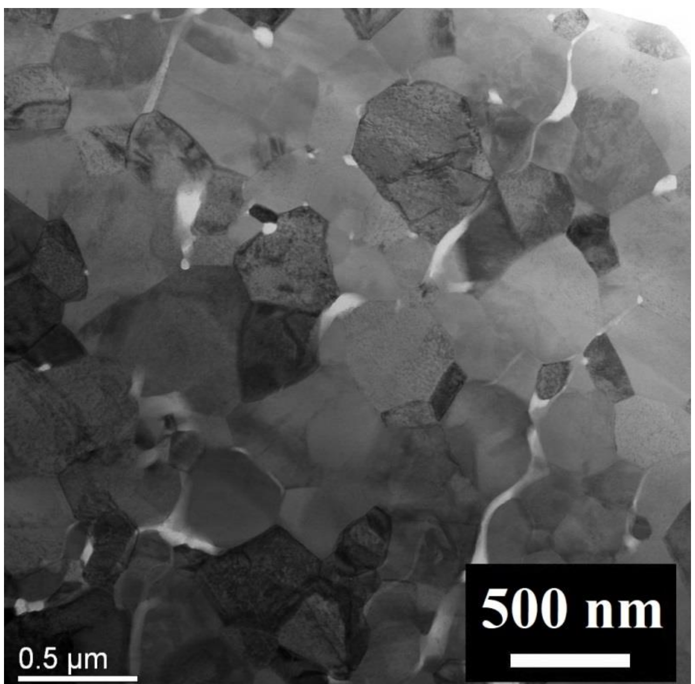
ZrO_2 without additives



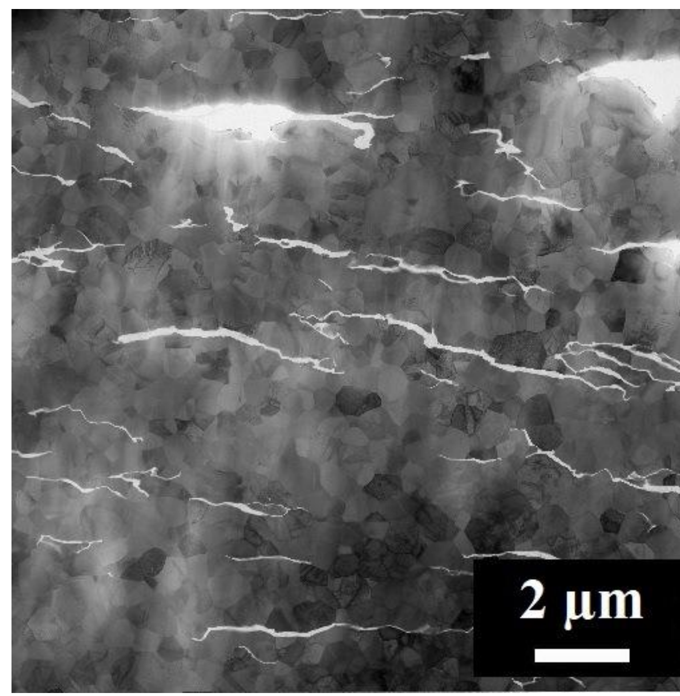
ZrO_2 + 1wt.% SWCNT



ZrO_2 + 1wt.% MWCNT

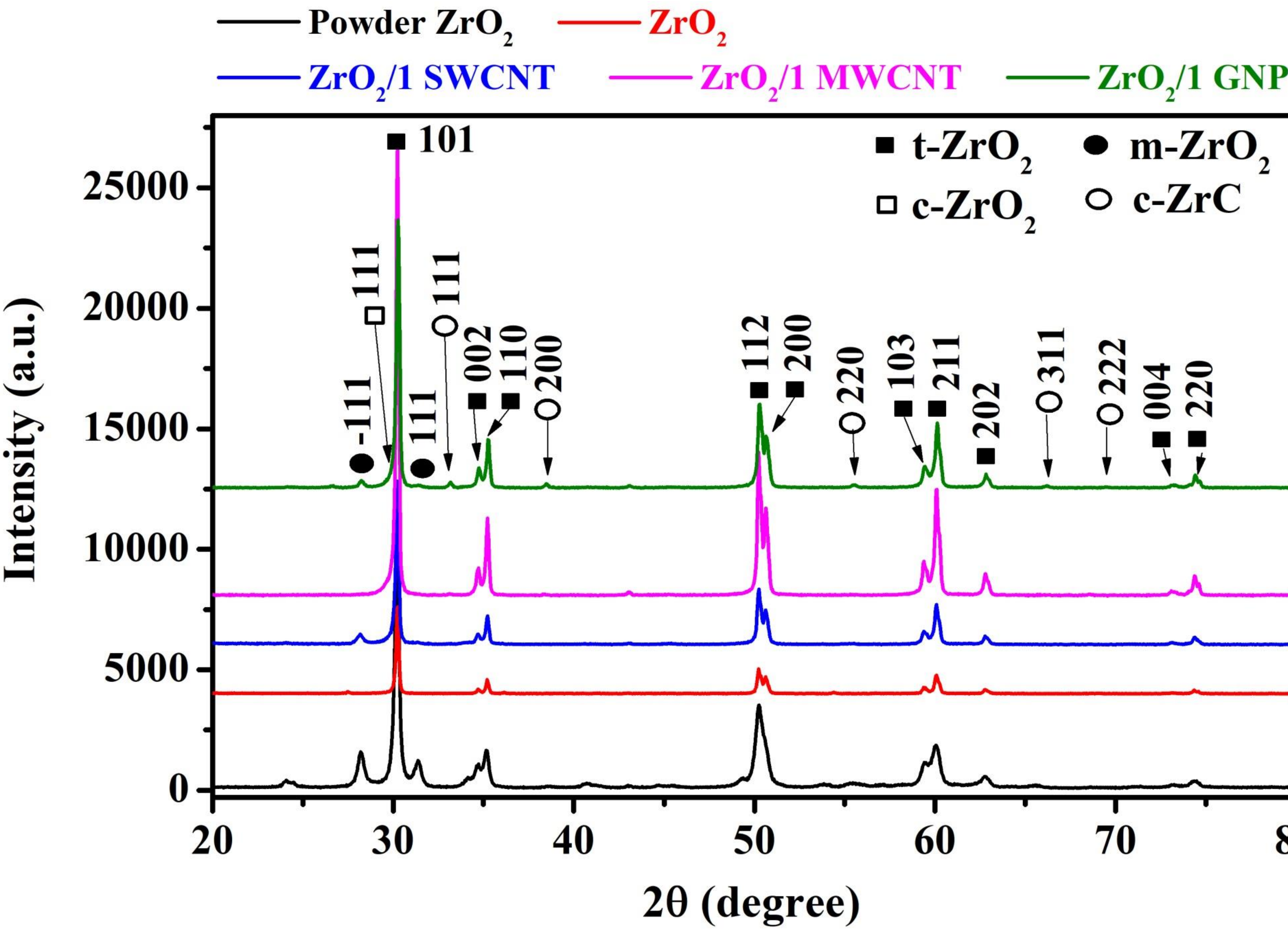


ZrO_2 + 1wt.% SWCNT



ZrO_2 + 1wt.% GNP

X-ray diffraction analysis of the samples

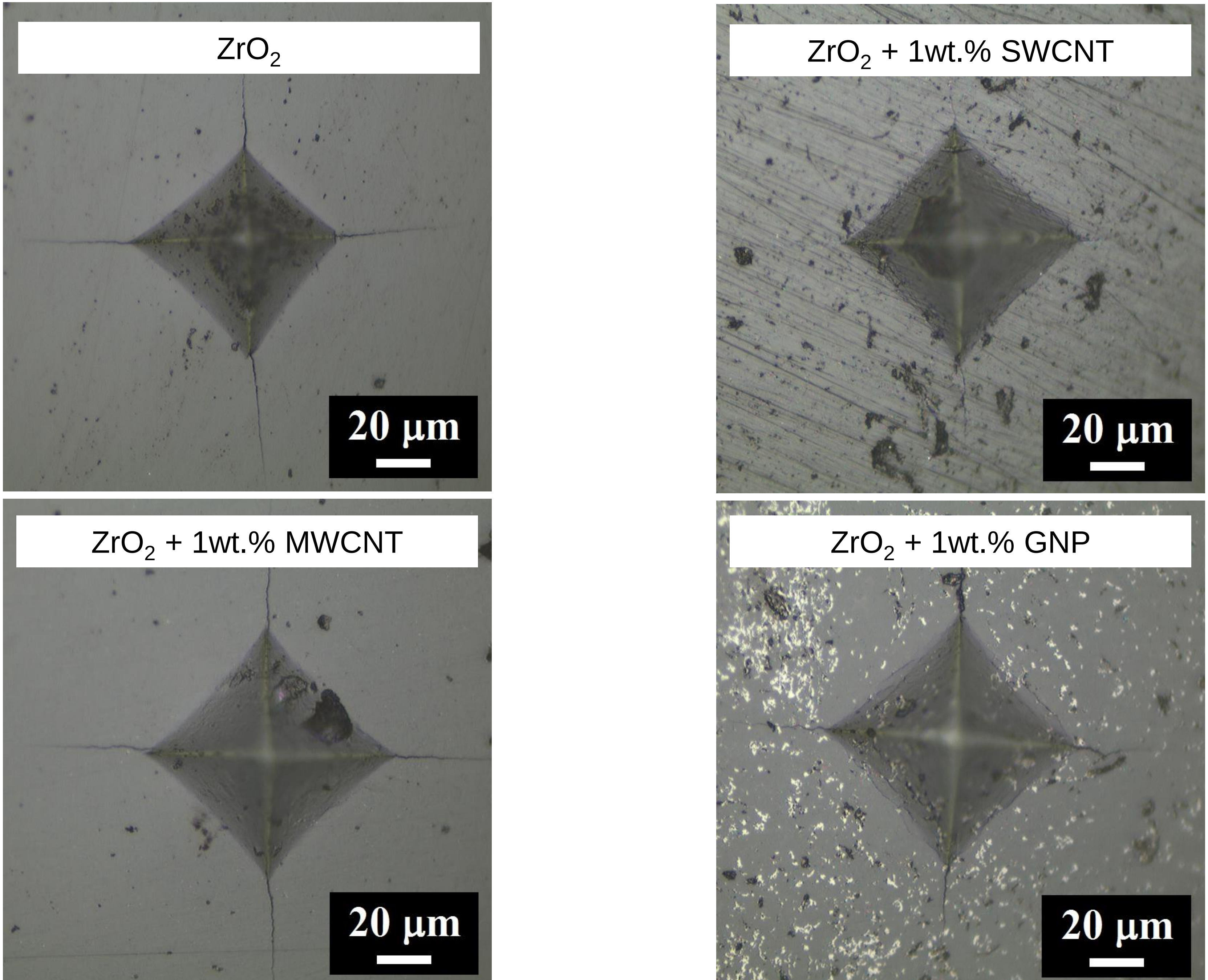


Properties of the studied samples

Sample	ρ_{rel} (%)	H_V (GPa)	K_{IC} (MPa·m$^{1/2}$)
ZrO_2	98.3	14.1 ± 0.3	4.0 ± 0.1
ZrO_2/SWCNT	95.5	11.6 ± 0.6	5.5 ± 0.4
ZrO_2/MWCNT	99.0	13.5 ± 0.3	4.3 ± 0.5
ZrO_2/GNP	99.4	13.1 ± 0.8	5.2 ± 0.6

The relative density of ZrO_2/SWCNT composite decreases from 98.3 % to 95.5 %, which is associated with the strong agglomeration of SWCNT, which prevents the rearrangement of ZrO2 nanoparticles during compaction/sintering, that increases the free volume. However, in composites with MWCNTs and GPNs, where reinforcing additives are not highly aggregated and have a lower specific surface area, the density increases, since CNMs can slip during compaction and fill pores. The microhardness of the composites is lower than that of ZrO_2 ceramics, because CNMs are a soft phase. The addition of MWCNTs as 1 wt.% almost has no effect on fracture toughness value. The fracture toughness increased from 4.0 to 5.5 MPa•m$^{1/2}$ for the composite ZrO_2/SWCNT and increased to 5.2 MPa•m$^{1/2}$ for the composite ZrO_2/GNP. From this viewpoint, GNPs seem more effective as reinforcement than SWCNTs and MWCNTs, because the ZrO_2/GNP composite has increased density and fracture toughness compared to ZrO_2 ceramics and in addition, the microhardness is not so much reduced in comparison with the ZrO_2/SWCNT composite.

Optical images of indentation and cracks on the samples



Conclusion

The influence of SWCNT, MWCNT and GNP on the microstructure, phase composition, densification, microhardness, fracture toughness and crack propagation of ceramic composites with a ZrO_2 matrix were analyzed. The relative density of composite with SWCNT decreases from 98.3 % to 95.5 %, however, in composites with MWCNTs and GPNs, where reinforcing additives are not highly aggregated and have a lower specific surface area, the relative density increases, since CNMs can slip during compaction and fill pores. It is established that SWCNTs and GNP partially limit the monoclinic–tetragonal transition occurring during high-temperature treatment of zirconia. It was found that GNP leads to the formation of a new phase, cubic zirconium carbide (c-ZrC). Was found that the microhardness composites decreased at the addition of carbon nanomaterials. Was shown that CNMs retain their structure after high-temperature sintering and they located at the zirconia grain boundaries. The fracture toughness of ZrO_2/SWCNT composite increased by 38 %, ZrO_2/MWCNT composite by 8 % and ZrO_2/GNP composite by 31 %, compared with ZrO_2 ceramics. Increased fracture toughness of composites is associated with the toughening mechanisms such as fiber pull-out, crack deflection and crack bridging and as well uncoiling and stretching of CNTs/GNPs.

Thanks for your attention!