MATERIALS.
TECHNOLOGIES.
DESIGN

УДК 539.4, P.A.C.S. 81.40.Np

Synergism of mechanisms for increasing fracture toughness of ceramics for medical use

Синергизм механизмов увеличения трещиностойкости керамики медицинского назначения

S. P. Buyakova [1]***, A. S. Buyakov*** [2]

С. П. Буякова [1]***, А. С. Буяков*** [2]

[1, 2] Institute of Strength Physics and Materials Science of Siberian Branch Russian Academy of Sciences, pr. Akademicheskii 2/4, Tomsk, 634055, Russia

[1] National Research Tomsk State University, Lenin Avenue 36, Tomsk, 634050, Russia

[1] National Research Tomsk Polytechnic University, Lenin Avenue 30, Tomsk, 634050, Russia

[1] sbuyakova@ispms.tsc.ru

[1, 2] Институт физики прочности и материаловедения СО РАН, Россия, 634055, Томск, пр. Академический, 2/4

[1] Национальный исследовательский Томский государственный университет, Россия, 634050, Томск, пр. Ленина, 36

[1] Национальный исследовательский Томский политехнический университет, Россия, 634050, Томск, пр. Ленина, 30

[1] sbuyakova@ispms.tsc.ru

ABSTRACT

The effect of multi-walled carbon nanotubes (MWCNTs) and hexagonal boron nitride (h-BN) inclusions on the fracture toughness of yttria-stabilized zirconia (YSZ) ceramics has been studied. It is shown that an increase in the MWCNTs and h-BN content has a positive effect on the K_{1C} of zirconia ceramics. The greatest increase in the fracture toughness of YSZ ceramics was observed with the introduction of hexagonal boron nitride particles. For YSZ ceramics, the K_{1C} value was ≈ 6.1 MPa·m$^{1/2}$, for ceramics with a 5 wt.% of h-BN K_{1C} ≈ 9.2 MPa·m$^{1/2}$. It was shown that an increase of the YSZ ceramics fracture toughness with the introduction of MWCNTs and h-BN, both and separately was provided by the combined action of several mechanisms of increasing the work of crack propagation. In addition, in all composites obtained in this work, the transformation of tetragonal ZrO_2 into monoclinic was observed.

KEYWORDS

Toughness and toughening mechanisms; ZrO_2 composites; medical ceramics.

АННОТАЦИЯ

Исследовано влияние многослойных углеродных нанотрубок (MWCNT) и включений гексагонального нитрида бора (h-BN) на вязкость разрушения керамики из диоксида циркония, стабилизированного оксидом иттрия (YSZ). Показано, что увеличение содержания MWCNT и h-BN положительно влияет на K_{1C} трещиностойкость циркониевой керамики. Наибольшее увеличение вязкости разрушения наблюдалось при введении частиц гексагонального нитрида бора. Для керамики YSZ значение K_{1C} составило ≈ 6,1 МПа·м$^{1/2}$, для керамики содержащей 5 вес.% h-BN K_{1C} ≈ 9,2 МПа·м$^{1/2}$. Показано, что увеличение трещиностойкости циркониевой керамики при введении MWCNT и h-BN, как по отдельности, так и одновременно, обеспечивалось совместным действием нескольких механизмов увеличения работы распространения трещин. Кроме того, во всех композитах, полученных в настоящей работе, наблюдалось превращение тетрагонального диоксида циркония в моноклинный.

КЛЮЧЕВЫЕ СЛОВА

Прочность и механизмы упрочнения; композиты ZrO_2; медицинская керамика.

Introduction

Ceramics based on yttria-stabilized zirconia (YSZ) are very attractive materials for many applications. Interest in YSZ ceramics is associated with a higher fracture toughness compared to other ceramic materials due to the tetragonal to monoclinic martensitic transformation in the stress field [1]. This phase transformation is accompanied by a shear strain of 0.16 and a volume expansion of 4%. The toughening mechanism is associated with the accommodation of transformation shape change [2]. In addition, zirconia-based ceramics have good ionic conductivity, stability at high temperatures, and resistance to many chemically aggressive environments. These properties allow the use of zirconia for the manufacture of solid oxide fuel cells, oxygen sensors, and membranes. Zirconia is actively used in medicine, for example, in surgical instruments, as bone tissue implants, or for dental prostheses. However, despite the existing successful experience in the use of zirconia-based ceramics, the range of its applications could be much wider if a higher fracture toughness is achieved.

Currently, various methods are known to increase the fracture toughness of ceramic materials. They consist in increasing the work of crack growth by introducing second phase inclusions into the ceramic matrix: particles, fibers or a layered structure can be created. The research development on the production and study of carbon nanotubes contributed to the appearance of experimental and theoretical studies of their effect on the mechanical properties of ceramics. It was assumed that reinforcing of ceramics with carbon nanotubes ensures the achievement of mechanical properties that are superior or similar to the mechanical properties of ceramics reinforced with ceramic whiskers. It is noted that the introduction of multi-walled carbon nanotubes (MWCNTs) into a ceramic matrix in some cases has a positive effect on the fracture toughness [3]. The fracture toughness of ceramics when they are reinforced with MWCNTs increases due to bridging, stretching, and collapsing during crack opening.

Another technique to increase fracture toughness is the introduction of low-modulus inclusions into the ceramic matrix. The increase of the fracture toughness of ceramics by the addition of inclusions with a significantly lower Young's modulus to the ceramic matrix referred to as the Cook-Gordon mechanism [4]. Contact of a crack tip with a relatively weak boundary leads to an increase of its curvature radius and subsequent bifurcation with a corresponding crack energy division. A necessary condition for the Cook-Gordon mechanism implementation and formation of a weak boundary is the difference in Young's modulus values of the matrix and the inclusion of more than five times. The main candidates for the role of low-modulus inclusions in the high-modulus ceramic matrix could be hexagonal boron nitride (h-BN) and carbon. Young's modulus of h-BN is 30 GPa, which is significantly less than Young's modulus of YSZ ceramics, which is more than 200 GPa [5].

The aim of the study presented in this work was to clarify the possibility of realizing several mechanisms of increasing the fracture toughness as a synergistic effect in YSZ ceramics. For this, multi-walled carbon nanotubes and hexagonal boron nitride particles, separately and together, were introduced into a YSZ ceramic matrix capable of manifesting a transformation toughening mechanism.

1. Materials and methods

Monolithic yttria-stabilized zirconia ceramics, composites 3YSZ–MWCNTs, 3YSZ–h-BN, and 3YSZ–MWCNTs–h-BN were studied. The content of MWCNTs, h-BN, or both MWCNTs and h-BN inclusions was 0.25; 0.5; 1; 3 and 5 wt.%. The specimens were designated as ZXM, where X indicates the inclusions type (C for MWCNTs, BN for h-BN, and BNC for both), and M indicates the wt.% of inclusions in the specimen.

Initial powder mixtures were prepared by ultrasonic-assisted mixing in the dimethylformamide media, followed by mechanical stirring in a ball mill with grinding bodies made of cubic zirconia according to the procedure described in [6].

Spark plasma sintering (SPS) of composites with MWCNTs, h-BN, or MWCNTs–h-BN content of 0.25, 1, and 0.5 wt.% was carried out at a temperature of 1300 °C for 30 minutes under a pressure of 40 MPa. Composites containing 3 and 5 wt.% of MWCNTs, h-BN or MWCNTs–h-BN were obtained by spark plasma sintering at a temperature of 1400 °C for 30 minutes under the same pressure.

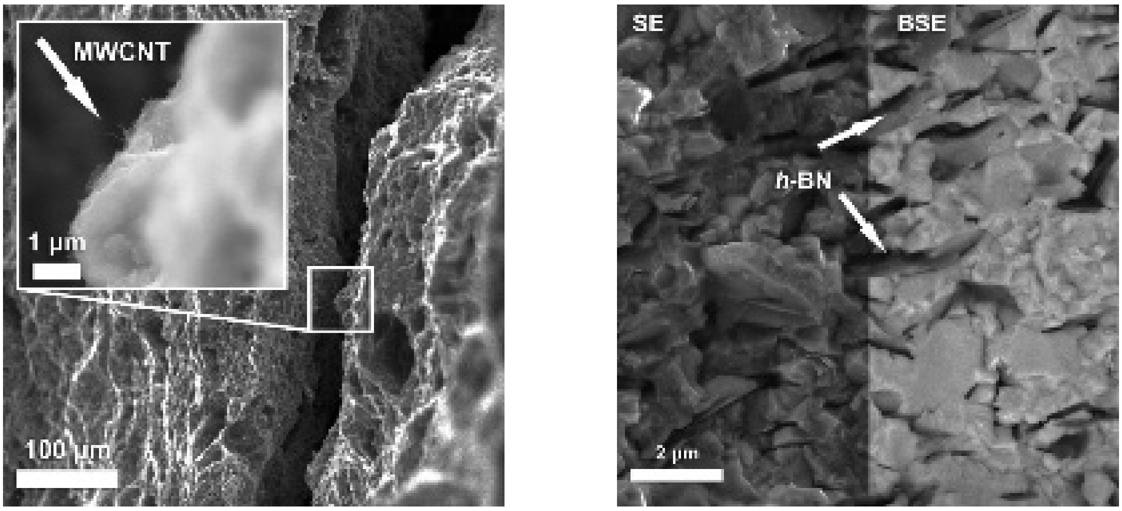
The Young's modulus of ceramic specimens was determined using nanoindentation technique with a three-sided pyramidal Berkovich diamond indenter. The fracture toughness was determined by measurement of the diagonal crack length from the Vickers imprint K_{IC}(INDENT) and by the Single-Edge-V-Notched beam (SENVB) method K_{IC}(SENVB). Calculation of K_{IC}(INDENT) by the total crack length was done according to the formula proposed in [7]. To assess the K_{IC}(SENVB) value the specimens were notched using a diamond charged cutting disk. After this, the notches were sharpened with the razor blade by polishing the notch tip using a diamond paste for final polishing with grit 0.25 μm. The three-point bending test was used to evaluate the fracture toughness, according to ASTM 1421 standard.

2. Results and discussion

In the ceramics obtained, the inclusions of carbon nanotubes and hexagonal boron nitride particles are very evenly distributed in the 3YSZ matrix. The Fig. 1, *a* shows an image of an open macrocrack formed after the destruction of the sample and an elongated carbon nanotube on its surface. The Fig. 1, *b* represents the fracture surface of the composite containing hexagonal boron nitride particles.

The relative density of composite specimens with a 0.25 wt.% and 5 wt.% content of MWCNTs was 99.8±0.01% and 99.2±0.05% respectively. Previous studies have shown that the density of ZC5 composites strongly depends not only on the sintering temperature but also on the particle size of the initial ceramic powder. The density of the 3YSZ–MWCNTs composites obtained in this work was higher than the density of the composites obtained in [8] by the SPS at a temperature of 1350 °C with equal content of carbon nanotubes.

Composites containing hexagonal boron nitride particles also had a high density. The relative density of ZBN0.25 and ZBN5 was 99.8±0.03% and 99.3±0.04% respectively. The density of the zirconia-based composite with a 5 wt.% h-BN is comparable with the density of the similar composite obtained in [9] by hot pressing at a temperature of 1650 °C. Of the composites obtained in this work, 3YSZ–MWCNTs–h-BN had the lowest density. The relative density of ZBNC0.25 composite was 99.5±0.02%, and the density of ceramics containing 5 wt.% of MWCNTs and h-BN was 97.3±0.08%.



a *b*

Fig. 1. Fracture surface of ceramic specimen 3YSZ with 5 wt.% of MWCNTs (*a*) and fracture surface of ceramic specimen 3YSZwith 5 wt.% of (h)-BN (*b*)

Рис. 1. Поверхность разрушения керамического образца, содержащего 5 вес.% MWCNT (*a*) и поверхность разрушения керамического образца, содержащего 5 вес.% h-BN (*b*)

The average grain size of 3YSZ ceramics was 0.69±0.23 μm. An increase in the MWCNTs/h-BN inclusions content was accompanied by a decrease in the average grain size of the 3YSZ ceramic matrix. The smallest grain size of zirconia ceramics had composites with MWCNTs. When 0.25 wt.% of MWCNTs were introduced into the zirconia matrix, the average grain size of 3YSZ was 0.71±0.12 μm, with an increase in the content of multi-walled carbon nanotubes to 5 wt.% the average grain size of the ceramic matrix decreased to 0.35±0.1 μm. In the ZBN0.25 composite, the average grain size of the zirconia matrix was 0.68±0.1 μm. With an increase of the h-BN content to 5 wt.% the average grain size of 3YSZ decreased to 0.52±0.02 μm. In the ZBNC5 composite, the average grain size of the ceramic matrix was 0.39±0.2 μm. A decrease in the zirconia grain size in composites with an increase in the content of hexagonal boron nitride particles and carbon nanotubes was reported in [10]. Thus, inclusions of MWCNTs and h-BN act as grain growth inhibitors.

Young's modulus of 3YSZ ceramics, measured by nanoindentation of the Berkovich pyramid, was E ≈ 197±20 GPa. Young's modulus of 3YSZ–MWCNTs composites increased with an increase in the number of carbon nanotubes. Young's modulus of composite ZC5 was 246 GPa.

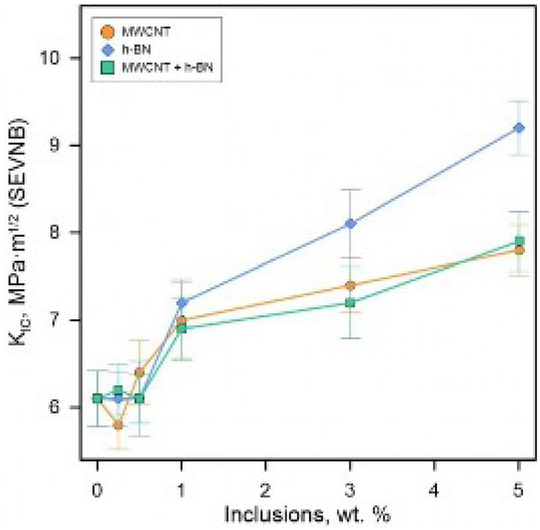
In studies [10] it was shown that the introduction of carbon nanotubes into tetragonal zirconia ceramics was accompanied by Young's modulus decreasing. As the reason for the observed decrease in Young's modulus when carbon nanotubes were introduced into the ceramic matrix, the authors highlighted, first of all, their uneven distribution in the ceramics, accompanied by the appearance of localized porosity. An increase in Young's modulus of ceramics with the introduction of carbon nanotubes is quite expected since E of CNTs is ≈ 0.9 TPa, which significantly exceeds Young's modulus of ceramic materials [8]. In 3YSZ–h-BN composites, on the contrary, an increase in the low-modulus hexagonal boron nitride content was accompanied by a decrease in Young's modulus. So, for example, for the 3YSZ composite – 5 wt.% h-BN demonstrated the E ≈ 175±10 GPa. Young's modulus of 3YSZ–MWCNTs–h-BN composites was slightly less than that of the composites with only multi-walled carbon nanotubes but higher than that of the composites with inclusions of hexagonal boron nitride. The E value of the composite with a total content of MWCNTs and h-BN being equal to 5 wt.% was 198±10 GPa.

The hardness Hv of 3YSZ ceramics was 12.2±0.15 GPa. The introduction of multi-walled carbon nanotubes into the 3YSZ ceramic matrix did not significantly affect its hardness, since the Hv of the ZC5 was 12.7±0.21 GPa. The hardness of 3YSZ–h-BN composites decreased with an increase in the content of hexagonal boron nitride. The Hv of the ZB5 was 9.4±0.13 GPa. The Hv of 3YSZ–MWCNTs–h-BN composites also decreased with increasing inclusion content: for the specimen containing 5 wt.% of inclusions Hv was 9.6±0.23 GPa.

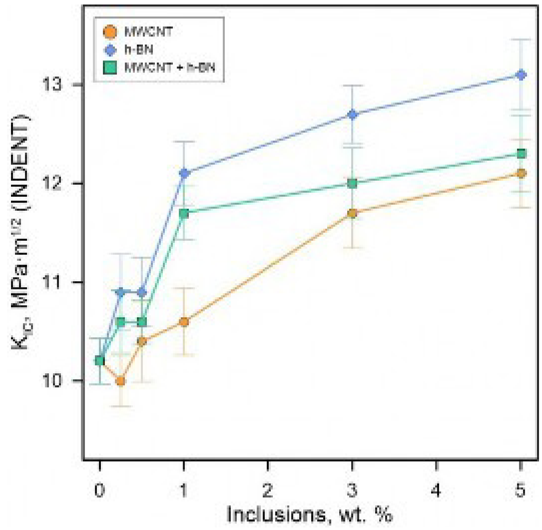
Fig. 2 shows the results of the fracture toughness determined by the total crack length of the Vickers indenter imprint and the SEVNB method for 3YSZ ceramics and 3YSZ–MWCNTs–h-BN composites. For 3YSZ ceramics, K_{1C}(INDENT), calculated from the total crack length, was 10.2±0.23 MPa·$m^{1/2}$, and K_{1C}(SEVNB) determined by the V-shaped notch method 6.1±0.32 MPa·$m^{1/2}$.

The presence of MWCNTs/h-BN inclusions in the 3YSZ ceramic matrix had a positive effect on the fracture toughness. The K_{1C} value for all the composites obtained in this work increased with an increase in the inclusions content. The highest fracture toughness had composites with inclusions of hexagonal boron nitride. When the content of h-BN in the ceramic matrix was 5 wt.% K_{1C}(SEVNB) was 9.8±0.31 MPa·$m^{1/2}$.

The fracture toughness of 3YSZ–MWCNTs composites with a nanotubes content of 1 wt.% or more was also higher than that obtained in this work for zirconia ceramics. For the ZC5 K_{1C}(SEVNB) was 7.8±0.29 MPa·$m^{1/2}$. For 3YSZ–MWCNTs–h-BN composites, the highest K_{1C}(SEVNB) was 7.9±0.34 MPa·$m^{1/2}$ with a total inclusion content of 5 wt.%.



a



b

Fig. 2. K_{1C} of 3YSZ–MWCNTs/h-BN composites determined by the SEVNB method (*a*) and by the total crack length from the Vickers indenter imprint (*b*)

Рис. 2. K_{1C} композитов 3YSZ–MWCNT/h-BN, определенный методом SEVNB (*a*) и по общей длине трещины по отпечатку индентора Виккерса (*b*)

Despite the similar tendencies of the K_{1C}(INDENT) and K_{1C}(SEVNB) values changes with an increase in the reinforcing inclusions content, K_{1C}(SEVNB) demonstrates more growth in the relative value. Researchers often argue about the application of one or another method for determining the fracture toughness of ceramic materials. The main argument for using the SEVNB technique is the often overestimated value of the fracture toughness, defined from the total crack length of the Vickers indenter imprint, which is due to the impossibility of reliable determination of the crack size.

From the results of studies of the effect of MWCNTs and h-BN inclusions on the fracture toughness of 3YSZ ceramics, it can be concluded that the most effective solution (of the considered) to increasing the crack propagation work is the introduction of hexagonal boron nitride low modulus particles into the ceramic matrix. The presence of relatively weak interphase interfaces in composites 3YSZ–h-BN is the reason for the deflection and bifurcation of cracks and as a consequence of the increase in the work of their propagation.

For the 3YSZ ceramics and 3YSZ–MWCNTs/h-BN composites obtained in this work, the K_{1C} values determined by the SEVNB method were less than the K_{1C} values calculated from the total crack length of the Vickers indenter imprint. Researchers often dismiss a significant difference between K_{1C}(INDENT) and K_{1C}(SEVNB), stating that indentation often shows unreasonably high fracture toughness.

For all composites obtained in this work, an increase in the inclusions content led to an increase in the fracture toughness. The development of cracks in composites with multi-walled carbon nanotubes was accompanied by “bridging”. In composites with hexagonal boron nitride inclusions, an increase in the fracture toughness is due to complete stop and/or cracks bifurcation at a relatively weak matrix-inclusion boundary (Cook-Gordon mechanism). However, the answer to the question of the synergy of the fracture toughness increasing mechanisms realized in the 3YSZ–MWCNTs–h-BN composites can be obtained from the analysis of the increment of monoclinic ZrO_2 in the fracture process.

Conclusion

The introduction of multi-walled carbon nanotubes into the 3YSZ ceramic matrix in an amount from 0.25 to 5 wt.% leads to an increase in Young's modulus and hardness of the resulting ceramic composite. The introduction of hexagonal boron nitride particles into the 3YSZ in the same amount, on the contrary, leads to a decrease in Young's modulus and hardness of ceramics. The introduction of both MWCNTs and h-BN into the ceramic matrix causes the synergistic effect neutralizing the separate influence of these inclusions on Young's modulus and hardness of the composite.

The introduction of both MWCNTs and h-BN into the 3YSZ ceramic matrix separately and together in an amount from 0.25 to 5 wt.% leads to an increase in the fracture toughness of the ceramic composite. The highest increase in fracture toughness is achieved with the introduction of h-BN particles into the 3YSZ ceramic matrix.

Acknowledgements

This research was carried out within the framework of Russian Academy of Sciences program FWRW-2021-0009. The results of EDS analysis were obtained the Central for Collective Use "Nanotech" at the ISPMS SB RAS (Tomsk, Russia).

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