Reactive sintering of TiB₂-SiC-CNT ceramics

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Abstract: TiB₂-SiC ceramics with multi-wall carbon nanotubes (MW-CNT) were reactively hot pressed at 1800°C and 30 MPa. Carbon nanotubes survived the process and could be clearly observed in the sintered ceramics. The in-situ exothermic reactions between TiC, B₄C and Si accelerated the densification and produced nonporous TiB₂-SiC ultrahigh-temperature ceramics within one minute at 1800 °C. Although the toughness of the ceramic was not significantly affected by the CNT addition, remaining around 6 MPa·m^{1/2}, the CNT presence resulted in a substantial improvement in TiB₂-SiC thermal shock resistance. The Vickers hardness decreased from 27GPa for the CNT-free matrix to 21GPa for ceramic with maximum CNT content (7.4 wt.%).

Keywords: carbon nanotubes; CNT composite; ultrahigh-temperature ceramics; borides; reactive sintering

1. Introduction

Composite materials based on transitional **metal** diboride and silicon carbide (**MeB₂-SiC**) possess an exceptional high-temperature stability in air and are known as ultra-high temperature ceramics (UHTC). UHTCs are used for scramjet engines, leading edges and nose-cones of hypersonic vehicles, heat exchangers, and advanced rocket motors [1, 2, 3, 4, 5, 6]. However, their high hardness and stiffness is also linked to a poor toughness and thermal shock resistance, which reduces the material performance in most high-temperature applications [7, 8].

At the same time, the most attractive characteristic of the materials – the melting points of the components averaging at around 3000°C – causes the main obstacle for their wider industrial utilization, as conventional manufacturing processes require long time sintering at very high temperatures. For example, bulk ZrB₂-based composites were hot pressed by Khoeini et al at 2000°C [9]. ZrB₂-SiC ceramics were hot pressed at 2200°C and 50 MPa for 2 hours by Chakraborty et al [10]. An addition of nanosized carbon allowed to densify ZrB₂-SiC powder at 1850°C and 20MPa in 60 min [11]. Almost non-porous TiB₂-SiC ceramics were sintered at 1980°C and 32 MPa for 10 min by King et al [12] and at 1800°C for 1 hour by Alavi et al [13]. The reduction of the **MeB₂-SiC** sintering temperature and time remains an outstanding challenge.

The use of modern sintering techniques such as spark-plasma sintering, as well as reactive hot pressing, allowed obtaining **MeB₂-SiC** ceramics at less demanding process conditions. For example, TiB₂-SiC green bodies being converted into almost nonporous TiB₂-SiC ceramics by SPS at 2000°C and 100 MPa for 3 min, has been reported by Singlard et al [14]. ZrB₂-SiC

materials were densified by means of SPS at 1800-1900°C and 35-40 MPa in 8 min [15, 16]. Reactive sintering of TiB₂-SiC materials via hot pressing of Ti-Si-B₄C-Ni precursors allowed Zhao et al. [17] to obtain nonporous TiB₂-SiC-based material at 1700°C and 32 MPa for 30 min, but the Ni-addition does not allow to classify these materials as UHTC. Chornobuk et al. [18] created TiB₂-SiC-C composites via hot pressing of a TiC-B₄C-Si precursor powder mixture at 2150°C for 8 min. Recent investigations of the TiC-B₄C high temperature interaction [19, 20, 21] however showed that the reaction can be finalized in 1-2 minutes at 1800°C.

It has been shown by Hasselman et al [22] that the thermal shock resistance of a ceramic can be improved by maximizing the fracture strength and thermal conductivity, which remains a challenge for MeB₂-SiC ceramics.

Carbon nanotubes are known as superior heat conductors ($k > 1500$ W/mK [23]) and have been used to reinforce nanocomposites [24]. There are a number of literature reports that demonstrate the successful incorporation of nanotubes into mullite [25, 26, 27] alumina [28, 29] at 1550°C and 1600°C, silicon nitride [30] at 1600°C, in silicon carbide [31] at 1800°C for 5 min, and TiN-based matrix [32]. One should however bear in mind that nanotubes might also react with the matrix at high sintering temperatures. To densify HfB₂-SiC and TiB₂-SiC composites higher temperatures are required that will concomitantly result in a reaction of the matrix with the CNTs. As mentioned in [33], despite the recent advances on embedding nanotubes in a ceramic matrix, the development of novel consolidation techniques that do not lead to CNT damage or dissolution while obtaining full densification remains a challenge.

The main purpose of the presented work is to demonstrate the reactive sintering technique development for the fast UHTC sintering and to report on successful incorporation of Carbon Nano Tubes into UHTC for the proven in this work thermal shock resistance enhancement.

2. Experimental procedure

Commercially available powders of TiB₂ (~30 µm), SiC (~30 µm), graphite (~20 µm), TiC (~70 µm), B₄C (~20 µm), and Si (~20 µm), all produced by Donetsk Reactive Factory, Ukraine, were used as starting powders for the TiB₂-SiC-C matrix. The material purity was around 99.00 at%.

The Multi-walled carbon nanotubes (MWCNTs) were synthesized at 900 °C by an Aerosol Chemical Vapor Deposition Technique (ACVD). TiB₂-SiC-C and TiC-B₄C-Si powder mixture compositions (See Table 1) were planetary ball milled in a zirconia jar with zirconia balls in air. Nanotubes in the amounts of 0, 1, 2, 4, and 8 wt.% were added and additionally planetary ball milled.

The starting powder compositions were chosen to correspond to the stoichiometry of the following reaction:

The Silicon content in the TiC-B₄C-Si mixture was chosen to create a slight carbon excess to allow preserving the nanotubes during in-situ reaction. A reference grade (TBSC) was conventionally hot pressed from a TiB₂-SiC-C powder mixture for comparison with the reactive hot pressed grades.

The ceramics were produced by the powder mixture hot-pressing at 1800 °C and 30 MPa in a graphite die. The die was heated with AC (50Hz) current in vacuum with the use of the hot-pressing equipment DCS-1 produced by SRC Synthesis (Kiev, Ukraine). The heating rate (after preheating at 500 °C for 20 min) was approximately 100 °C/min. The isothermal dwelling time for the different ceramics is presented in Table 1. The hot pressed specimens were in the form of discs of 10 mm diameter.

The bulk density of the sintered ceramics were measured using the Archimedes method and the theoretical densities (ρ_{th}) were estimated according to the rule of mixtures based on the right-hand side of reaction (1) and the precursor CNT content. The crystalline phases were determined by X-Ray Diffraction (XRD). Analysis of the microstructure was performed by Scanning Electron Microscopy (SEM). For SEM analysis, samples were cleaved as this allowed to side-step polishing artefacts in material with a high hardness variation. Vickers hardness measurements were performed with a load of 49 N and 98 N for 20s on polished surfaces. The fracture toughness was estimated by measuring the crack lengths generated by the Vickers indentations with a load of 98 N. The toughness was calculated according to the formula of Evans and Charles [34].

Thermal shock crack growth was explored according to the indentation-quench method, as presented in [35]. The disk specimens were polished and indented using a Vickers pyramidal indenter with a load of 49 N for 10 s. Five indentations were made on each specimen. Four cracks were formed near each indentation, so a total of 20 cracks per sample were measured. The samples were heated to a selected temperature of 200, 300, 400, and 500°C in a furnace in air for 10 min and then quenched into a water bath at room temperature (20°C). The radial crack lengths of each indentation were measured before and after each quenching procedure using an optical microscope. The crack growth was expressed as percentage to the previous thermal shock step as:

$$(c_i - c_{i-1})/c_{i-1} \times 100\% \quad (2)$$

with i , the number of consequent quenching procedures. The average crack growth for each material was estimated as a function of the temperature interval.

3. Experimental results and discussion

3.1. The influence of in situ reactions on TiB₂-SiC-C densification kinetics

The TBSC and TS01 powder mixtures contained the same molar amounts of Ti, B, Si, and C. The influence of reactive sintering versus conventional powder mixture densification was investigated as the green bodies were processed and sintered with the same parameters (temperature, time and pressure, see Table 1). Fig.1 shows both quantitative and qualitative differences in the densification kinetics of both powder mixtures.

The consolidation of non-reactive TBSC powder has no peculiarities. Densification starts around 1300°C and accelerates gradually with temperature approximating 0.25 mm/min at 1800°C. The densification rate decreased after 2 minutes at 1800°C with a sample density after 8 min hot pressing of only around 73%. In contrast, the densification of the reactively pressed TS01 powder mixture occurred in two clear stages. The first stage begins already at 1050°C and stops after a minute at around 1200°C. The second stage starts at 1400°C and lasts approximately 2 min. The maximum consolidation rates in the first and second stage were 2.5 and 1 mm/min respectively and were a factor of 10 larger than for the TBSC powder at 1800°C (See Fig.1b). The reactively hot pressed TS01 reached maximum densification already after 1 minute at 1800°C. As the material manufacturing processes were identical for both samples, the differences in consolidation behaviour should be attributed to the in-situ chemical transformation during reactive hot pressing.

As shown in Fig. 2, the sintering of the 2TiC-B₄C-2.5Si powder mixture at 1800°C for 1 min led to the disappearance of the original phases, and the formation of new phases like TiB₂, SiC and graphite. This proceeds in accordance with reaction (1). Annealing of the same powder compact at only 1200°C (the temperature at which the first densification stage was completed, see Fig.1) resulted in the formation of titanium diboride and silicon carbide, along with some residual titanium carbide. However, the molar ratio of product phase content changed substantially.

Quantitative XRD analysis showed that annealing of 2TiC-B₄C-2.5Si powder at 1200°C resulted in a TiB₂ to SiC molar ratio around 2.2. As the sintering temperature rose to 1800°C, the ratio changed to 1.2. This is in agreement with reaction (1). As shown in [36], the high temperature interaction between titanium and boron carbides starts with the nucleation of TiB₂ on the TiC surface, which causes the first densification step (See Fig.1), similar to that presented in [19] for a 2TiC-B₄C composition. Silicon binds some carbon emerging from the reacting phases, but the process stops as the solid reaction product, i.e. TiB₂, separates the reactants.

The sintering temperature exceeded 1400°C accelerated boron carbide decomposition [19], and leads to silicon melting ($T_m=1414^\circ\text{C}$ [37]). Both processes improve boron and silicon transport and intensify the conversion reaction, which is the reason for the second consolidation step.

It should be noted that the actual density of the reactively hot pressed ceramics is higher than the theoretical density calculated assuming the rule of mixtures (See Table 2). The result is similar to that presented in [19]. The discrepancy of 5% could hardly be explained by the impurities or errors. The theoretical value in Table 2 was calculated presuming a precise stoichiometric composition of both initial and product phases in reaction (1). However, it is well known that titanium carbide can have a carbon under stoichiometry of 2-40 % [38, 39]. Henceforth, reaction (1) should be changed into:

This means that the nonporous reactively pressed material density can change from 3.79 g/cm³ ($x = 0$) to 3.86 ($x = 0.25$), actually reaching the experimental values (Table 2).

The densification (see Fig.1.) of 2TiC-B₄C-2.5Si powder stopped after not more than 1 minute at 1800°C. The density and mechanical characteristics of TS01 (sintered for 8 min) and TS02 (sintered for 1 min) are within the error margin (See Table 2). It means that 1 min of hot pressing at 1800°C was sufficient to fully densify the 2TiB₂-2.5SiC-0.5C material via the reactive sintering procedure. These processing conditions were therefore also selected for the CNT-containing ceramic synthesis.

3.2. Structure and properties of TiB₂-SiC-C-CNT composites

Table 3 shows that all CNT-containing ceramics had reached full density after 1 min reactive hot-pressing. However, the introduction of nanotubes into 2TiC-B₄C-2.5Si powder had a clear impact on the green body densification kinetics, as shown in Fig. 3. The sample thickness at the beginning of the process decreased with increasing nanotube content, revealing the increasing efficiency of the cold pressing because of CNT-induced intergranular slip. On the other hand, the CNT dispersion reduces the first consolidation stage speed (See Fig. 3b) preventing the precursor contacts and suppressing the reaction. However, the second densification stage was not affected by the nanotubes demonstrating that the CNTs have no influence on gas and liquid phase atomic transport.

Fig. 4 shows SEM images of the fracture surface of TN04 with the highest CNT content. The microstructure contains ceramic grains and features which can only be CNTs. As we have used a CNT containing powder mixture, mostly multiwall CNTs with an external diameter around 100 nm are observed in the sintered ceramic. Few probably single wall nanotubes can also be seen with a diameter of a few tens of nanometers. Essentially, this confirms the CNT survival during material consolidation and synthesis at 1800°C. Moreover, the presented fast reactive sintering process demonstrated the possibility to modify ultrahigh temperature MeB₂-SiC ceramics with carbon nanotubes.

The micro hardness of the ceramics decreased with increasing nanotube content, while the crack resistance remained constant. TN02 with 4.5 vol.% of CNTs presents the only exception of the tendency having essentially a higher hardness and lower toughness (29.3 GPa and 4.5 MPa·m^{1/2}, See Table 3). The reason for this exception is not clear.

A possible explanation for the nanotube unaffected material toughness is as follows. A crack expanding inside the material creates micro stresses, which are of the order of the interatomic bond strengths at the crack tip. The interatomic strength can be approximately estimated as 10% of the material Young's modulus [40] and for TiB₂ and SiC approximates 45 GPa and 54 GPa respectively correlating with the CNT strength (20-50 GPa [33]). Therefore, when a crack front meets a nanotube solidly connected to the matrix, the crack tip microstresses cleave the CNT as easy as the matrix phases. Strength and toughness improvement can be achieved only if the CNT-matrix interface is relatively weak, allowing crack bridging and nanotube pull out of the matrix increasing the crack resistance and material fracture energy. It is speculated that the functionalization of CNTs can lead to a lower interaction with the matrix and improve the crack resistance by establishing CNT pull-out.

The SEM image of the TN04 fracture surface (See Fig.4) presents an essential number of nanotubes between the matrix grains, but no CNTs perpendicular to the surface, i.e. no unequivocal evidence for CNT pull-out. The latter means that nanotubes were strongly connected to the matrix grains and did not affect the fracture toughness. On the other hand, this strong connection accompanied by the fine nanotube distribution within the matrix can be an advantage from the point of view of thermal conductivity and the material stability under severe temperature variations.

The indentation-quench technique presented in [35] is an effective method for brittle material thermal shock behaviour assessment. The crack growth in this case is due to consequent quenching from increasing temperatures. It has been done by optical microscopy in our case (see Fig.5).

The behaviour of the nanotube-free ceramic (See Fig. 6) was slightly better than for ZrB₂-SiC-AlN ceramics in which the crack propagation at $\Delta T = 400^\circ\text{C}$ reached 120% [35]. As it is evident from Fig.6, the addition of CNTs to the TiB₂-SiC-C ceramics improved the thermal shock resistance substantially. The thermal shock crack propagation decreased by a factor of 3 for the ceramics containing 8.6 and 15.9 vol.% nanotubes. It can be speculated at this point that the increased thermal shock resistance is directly related to the enhanced thermal conductivity of the ceramic composites containing nanotubes. The thermal shock resistance of a brittle material when satisfying the criterion of the thermal stresses not exceeding the material fracture stress (σ_f) can be estimated according to Hasselman et al [22] as:

$$R' = \frac{\sigma_f(1-\nu)k}{\alpha E} \quad (4)$$

where ν , α , k , and E are the Poisson's ratio, thermal expansion coefficient, thermal conductivity and Young's modulus respectively. It is evident that the increased thermal conductivity directly increased the thermal shock resistance.

The developed reactive sintering approach and thermal shock resistance improvement by the incorporation of CNTs possibly can be applied to produce ultra-high temperature materials based on other MeB₂-SiC systems (Me = Zr, Hf).

4. Conclusions

In the present work, a reactive sintering approach for the full densification of TiB₂-SiC-C ceramics has been developed starting from TiC-B₄C-Si powder mixtures. Full densification is achieved by hot pressing at 1800°C for 1 min at 30 MPa in vacuum. Carbon nanotubes have been added to the green body and evidently survived the sintering conditions. The addition of CNTs modified the densification process during synthesis and reduced the material hardness. The crack resistance of the material is not affected by the CNT addition and nanotube cleavage was observed during crack propagation. The fast hot pressing at relatively low temperature with an in-situ reaction forming carbon facilitated the CNTs to survive the densification procedure. The higher thermal conductivity of the ceramic upon nanotube addition substantially improved the ceramic matrix thermal shock resistance.

References

1. Monteverde F., Savino R., Fumo M.D.S., Maso A.D. Plasma wind tunnel testing of ultra-high temperature ZrB₂-SiC composites under hypersonic re-entry conditions // *Journal of the European Ceramic Society*, Vol. 30, No. 11, 2010. pp. 2313-2321.
2. Kou H., Li W., Cheng T., Li D., Wang R. Thermal shock resistance of ultra-high temperature ceramics under // *Applied Thermal Engineering*, Vol. 110, 2017. pp. 1247-1254.
3. Nekahi S., Vajdi M., Moghanlou F.S., Vaferi K., Motallebzadeh A., Özen M., Aydemir U., Sha J., Asl M.S. TiB₂-SiC-based ceramics as alternative efficient micro heat exchangers // *Ceramics International*, Vol. <https://doi.org/10.1016/j.ceramint.2019.06.150>, in press 2019.
4. Vaferi K., Nekahi S., Vajdi M., Moghanlou F.S., Shokouhimehr M., Motallebzadeh A., Shad J., Asl M.S. Heat transfer, thermal stress and failure analyses in a TiB₂ gas turbine stator blade // *Ceramics International*, Vol. <https://doi.org/10.1016/j.ceramint.2019.06.184>, in press 2019.
5. Moghanlou F.S., Vajdi M., Sha J., Motallebzadeh A., Shokouhimehr M., Asl M.S. A numerical approach to the heat transfer in monolithic and SiC reinforced HfB₂, ZrB₂ and TiB₂ ceramic cutting tools // *Ceramics International*, Vol. 45, No. 13, 2019. pp. 15892-15897.
6. Moghanlou F.S., Vajdi M., Sha A., Motallebzadeh J., Shokouhimehr M., Asl M.S. Numerical analyses of heat transfer and thermal stress in a ZrB₂ gas turbine stator blade // *Ceramics International*, Vol. <https://doi.org/10.1016/j.ceramint.2019.05.344>, in press 2019.
7. Cheng T., Li W., Fang D. Thermal Shock Resistance of Ultra-High-Temperature Ceramics // *AIAA Journal*, Vol. 51, No. 4, 2013. pp. 840-848.
8. Li W., Yang F., Fang D. Thermal shock modeling of Ultra-High Temperature Ceramics under // *Computers and Mathematics with Applications*, Vol. 58, 2009. pp. 2373-2378.
9. Khoeini M., Nemati A., Zakeri M., Asl M.S. Pressureless sintering of ZrB₂ ceramics codoped with TiC and graphite // *International Journal of Refractory Metals and Hard Materials*, Vol. 81, 2019. pp. 189-195.
10. Chakraborty S., Debnath D., Mallick A.R., Das P.K. Mechanical and Thermal Properties of Hot-Pressed ZrB₂-SiC // *Metallurgical and Materials Transactions A*, Vol. 45A, 2014. pp. 6277-6284.
11. Asl M.S., Nayeji B., Kakroudi M.G., Shokouhimehr M. Investigation of hot pressed ZrB₂-SiC-carbon black nanocomposite by scanning and transmission electron microscopy // *Ceramics International*, Vol. <https://doi.org/10.1016/j.ceramint.2019.05.211>, in press 2019.
12. King D.S., Fahrenholtz W.G., Hilmas G.E. Silicon carbide-titanium diboride ceramic composites // *Journal of the European Ceramic Society*, No. 33, 2013. pp. 2943-2951.
13. Alavi S.H., Baharvandi H.R., Abdizadeh H. Densification and mechanical properties of TiB₂-SiC // *International Journal of Modern Physics: Conference Series*, Vol. 05, 2012. pp. 598-606.
14. Singlard M., Tessier-Doyen N., Chevallier G., Oriol S., Fiore G., Vieille B., Estournès C., Vardelle M.,

- Rossignol S. Spark plasma sintering and mechanical properties of compounds in TiB₂-SiC pseudo-diagram // *Ceramics International*, Vol. 44, No. 18, 2018. pp. 22357-22364.
15. Mohammadpour B., Ahmadi Z., Shokouhimehr M., Asl M.S. Spark plasma sintering of Al-doped ZrB₂-SiC composite // *Ceramics International*, Vol. 45, No. 4, 2019. pp. 4262-4267.
  16. Asl M.S., Nayeibi B., Motallebzadeh A., Shokouhimehr M. Nanoindentation and nanostructural characterization of ZrB₂-SiC composite doped with graphite nano-flakes // *Composites Part B: Engineering*, Vol. 175, 2019. pp. 1359-8368.
  17. Zhao G., Huang C., Liu H., Zou B., Zhu H., Wang J. Microstructure and mechanical properties of TiB₂-SiC ceramic composites by Reactive Hot Pressing // *Int. Journal of Refractory Metals and Hard Materials*, No. 42, 2014. pp. 36-41.
  18. Chornobuk S., O. Popov V.M. Structure formation kinetics and micromechanical characteristics evolution of reactively sintered materials of TiB₂-SiC-C system // *Deformation and fracture of materials*, No. 11, 2009. pp. 15-18.
  19. Popov O., Chornobuk S., Vishnyakov. V. Structure formation of TiB₂-TiC-B₄C-C hetero-modulus ceramics via reaction hot pressing // *International Journal of Refractory Metals and Hard Materials*, No. 64, 2017. pp. 106-112.
  20. Popov O., Klepko A., Lutsak E. The influence of high pressure on TiC-B₄C reaction kinetics // *International Journal of Refractory Metals and Hard Materials*, Vol. 75, 2018. pp. 234-237.
  21. Popov O., Vishnyakov V., Chornobuk S., Totsky I., Plyushchay I. Mechanisms of TiB₂ and graphite nucleation during TiC-B₄C high temperature interaction // *Ceramics International*, Vol. <https://doi.org/10.1016/j.ceramint.2019.05.209>, in press 2019.
  22. Hasselman D.P.H., Becher P.F., Mazdiyasni K.S. Analysis of the Resistance of High-E, Low-E Brittle Composites to Failure by Thermal Shock // *Z. Werkstofftech*, No. 11, 1980. pp. 82-92.
  23. Martin-Gallego M., Verdejo R., Khayet M., Ortiz de Zarate J.M., Essalhi M., Lopez-Manchado M.A. Thermal conductivity of carbon nanotubes and graphene in epoxy nanofluids and nanocomposites // *Nanoscale Research Letters*, No. 6, 2011. pp. 610-617.
  24. Ahmad I., Yazdani B., Zhu Y. Recent Advances on Carbon Nanotubes and Graphene Reinforced Ceramics Nanocomposites // *Nanomaterials*, No. 5, 2015. pp. 90-114.
  25. Yasin Orooji E.G.M.M.M.D.R., Alizadeh M., Asl M.S., Ebadzadeh T. Preparation of mullite-TiB₂-CNTs hybrid composite through spark plasma sintering // *Ceramics International*, Vol. 45, No. 13, 2019. pp. 16288-16296.
  26. Orooji Y., Derakhshandeh M.R., Ghasali E., Alizadeh M., Asl M.S., Ebadzadeh T. Effects of ZrB₂ reinforcement on microstructure and mechanical properties of a spark plasma sintered mullite-CNT composite // *Ceramics International*, Vol. 45, No. 13, 2019. pp. 16015-16021.
  27. Orooji Y., Alizadeh A., Ghasali E., Derakhshandeh M.R., Alizadeh M., Asl M.S., Ebadzadeh T. Co-reinforcing of mullite-TiN-CNT composites with ZrB₂ and TiB₂ compounds // *Ceramics International*, Vol. <https://doi.org/10.1016/j.ceramint.2019.07.072>, in press 2019.
  28. Leonov A.A., Khasanov A.O., Danchenko V.A., Khasanov O.L. Spark plasma sintering of ceramic matrix composite based on alumina, reinforced by carbon nanotubes // *IOP Conf. Series: Materials Science and Engineering*, No. 286, 2017. P. 012034.
  29. Hanzel O., Sedláček J., Sajgalík P. New approach for distribution of carbon nanotubes in alumina matrix // *Journal of the European Ceramic Society*, Vol. 34, 2014. pp. 1845-1851.
  30. Matsuoka M., Tatami J., Wakihara T., Komeya K., Meguro T. Improvement of strength of carbon nanotube-dispersed Si₃N₄ ceramics by bead milling and adding lower-temperature sintering aids // *Journal of Asian Ceramic Societies*, No. 2, 2014. pp. 199-203.
  31. Morisada Y., Miyamoto Y., Takaura Y., Hirota K., Tamari N. Mechanical properties of SiC composites incorporating SiC-coated multi-walled carbon nanotubes // *International Journal of Refractory Metals & Hard Materials*, Vol. 25, 2006. pp. 322-327.

32. Delbari S.A., Nayebi B., Ghasali E., Shokouhimehr M., Asl M.S. Spark plasma sintering of TiN ceramics codoped with SiC and CNT // *Ceramics International*, Vol. 45, No. 3, 2019. pp. 3207-3216.
33. Cho J., Boccaccini A.R., Shaffer M.S.P. Ceramic matrix composites containing carbon nanotubes // *J Mater Sci*, No. 44, 2009. pp. 1934-1951.
34. Evans A.G., Charles E.A. Fracture toughness determinations by indentation // *J Am Ceram Soc*, Vol. 59, 1976. pp. 371-372.
35. Liang J., Wang Y., Fang G., Han J. Research on thermal shock resistance of ZrB₂-SiC-AlN ceramics using an indentation-quench method // *Journal of Alloys and Compounds*, Vol. 493, 2010. pp. 695-698.
36. Popov O., Vishnyakov V. Fracture toughness in some hetero-modulus composite carbides: carbon inclusions and voids // *Advances in Applied Ceramics*, Vol. 116, 2017. pp. 61-70.
37. // NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry/>.
38. Chien F.R., Nutt S.R., Cummings D. Defect structures in single crystal TiC // *Adv. Apl. Ceram.*, Vol. 68, 1993. pp. 325-348.
39. Zhao Q., Wu J., Chaddha A., Chen H., Parsons J., Downham D. Defect structure in single crystal titanium carbide // *J. Mater. Res.*, Vol. 9, No. 8, 1994. pp. 2096-2101.
40. Bartenev G.M., Zuyev Y.S. *Strength and failure of visco-elastic materials*. Oxford: Pergamon Press, 1968. 434 pp.

Tables

Table 1. Starting powder compositions and sintering time at 1800°C and 30 MPa

#	SiC, wt.%	TiB ₂ , wt.%	B ₄ C, wt.%	TiC, wt.%	Graphite, wt.%	Si, wt.%	CNT, wt.%	t, min
TBSC	48.2	47.6	-	-	4.3	-	-	8
TS01	-	-	49	22.5	-	28.5	-	8
TS02	-	-	49	22.5	-	28.5	-	1
TN01	-	-	48.5	22.3	-	28.2	1	1
TN02	-	-	48	22.0	-	28.0	2	1
TN03	-	-	47	21.6	-	27.6	3.8	1
TN04	-	-	45.4	20.8	-	26.4	7.4	1

Table 2. Density and mechanical properties of the hot pressed ceramics

Sample #	t (min)	ρ_{th} (g/cm ³)	ρ (g/cm ³)	ρ/ρ_{th} (%)	H _v (GPa)	K _{1C} (MPa·m ^{1/2})
TBSC	8	3.79	2.76	73	-	-
TS01	8	3.79	3.88	103	27.8 ± 2.0	5.8 ± 0.8
TS02	1	3.79	3.87	102	27.4 ± 1.8	5.9 ± 0.7

Table 3. Mechanical properties and densities (theoretical and measured)

#	CNT content (vol.%)	ρ_{th} (g/cm ³)	ρ (g/cm ³)	H _v (GPa)	K _{1C} (MPa·m ^{1/2})
TS02	0	3.79	3.87	27.4 ± 1.8	5.9 ± 0.7
TN01	2.3	3.74	3.80	26.3 ± 1.5	5.8 ± 0.5
TN02	4.5	3.69	3.75	29.3 ± 2.1	4.5 ± 0.6
TN03	8.6	3.60	3.69	23.3 ± 1.2	6.2 ± 0.4
TN04	15.9	3.44	3.52	21.4 ± 1.2	5.9 ± 0.5

Figures

Fig. 1. The densification kinetics of TBSC and TS01: a) compact thickness (H) and sintering temperature (T) versus processing time; b) densification rate (dH/dt) versus sintering temperature.

Fig. 2. XRD patterns of 2TiC + B₄C + 2.5Si powder mixture (the initial composition of TS01 and TS02, Table.1) after 1 minute hot pressing at 1200°C and at 1800°C.

Fig. 3. Densification curves of the reactive sintered CNT-free and CNT containing powder compacts (a) and selected densification rate curves (b).

Fig. 4. SEM images of a TN04 (15.9 vol.% of CNT) fractured surface revealing the presence of CNTs.

Fig. 5. Image of indentation and cracks on TiB₂-SiC-CNT sample. CNT concentration 2%, indentation load 5kg. a) - indentation optical image, b) – the measured feature sizes.

Fig. 6. Average percentage growth of indentation cracks versus quenching temperature difference (ΔT) for ceramics with different CNT volume content (TS02, TN01, TN03 and TN04)