DOI: 10.21062/mft.2020.046 © 2020 Manufacturing Technology. All rights reserved. http://www.journalmt.com

Hot Pressing of Boron Carbide Based Ceramic Composites

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Ceramic composite materials based on boron carbide were hot pressed utilising in situ reaction of boron carbide powder with 40 wt.% of titanium dioxide sintering additive. The samples were prepared at sintering temperature of 1850 °C, pressure of 35 MPa, and time of 60 min in vacuum atmosphere of about 20 Pa. Optimisation of sintering regime concentrating on both heating stage of sintering and application of pressure enabled to prepare fully dense ceramic composite materials composed of boron carbide matrix with 29.5 vol.% of titanium diboride secondary phase. The ceramic composite reached average density of 99.31 %, hardness of 29.8 GPa, and fracture toughness of 6.9 MPa.m$^{1/2}$.

Keywords: boron carbide, ceramic composite, sintering, microstructure

1 Introduction

Boron carbide (B_4C) based ceramics and ceramic composites with B_4C matrix have been intensively studied materials because of their extraordinary properties that stem from their microstructure. Boron carbide is according its mainly covalent bonds extremely hard, corrosion resistant and wear resistant material at both room and elevated temperatures. Low density, high Young modulus and high absorption cross section for neutrons are other important properties of B_4C. One important advantage in comparison with many ceramic materials is good electric conductivity, which enables to form products from B_4C by electrical discharge machining [1-4]. Based on its properties B_4C ceramic and ceramic composites are promising material for production parts working in demanding working conditions. Extraordinary hardness predestines B_4C for applications requiring high abrasive and erosive wear resistance such as sand-blast nozzles and water jet nozzles. Small density and high modulus of elasticity make B_4C based ceramics a perspective material for light armour such as bullet-proof vests and aircraft applications. High active cross section of B_4C for neutrons absorption can be utilised in nuclear technique [3-6].

The potential of B_4C is decreased by both difficult sinterability and low fracture toughness of this ceramic material. Difficult sinterability of B_4C stems from the low self-diffusion coefficients in this ceramic system. Relatively high temperatures, above 2300 °C, are necessary to achieve compacts with the density near to the theoretical density of 2.52 g.cm^{-3}. However, the sintering of B_4C ceramics at temperatures above 2000 °C is accompanied with particle coarsening in ceramic compacts which decrease mechanical properties such as strength, hardness and fracture toughness. However, the fracture toughness of B_4C based ceramics must be improved for successful application of this ceramic material [3, 7-10].

Both problems of preparation of B_4C based ceramics decreasing of sintering temperature and increasing of fracture toughness of samples can be solved by sintering of ceramic composite systems. Selection of suitable composite systems enables creation of new phases in situ during sintering process of B_4C powder with proper sintering additives. Sintering additives improve densification and influence microstructure and mechanical properties of boron carbide based composite materials because of creation of secondary phases. The secondary phases are significant mainly for increasing of fracture toughness, which is critical for B_4C based ceramic materials because it reaches values only from 2.2 to 3.7 MPa.m$^{1/2}$. Hardness of B_4C based ceramic composite usually decreases, because phases with lower hardness create compared to B_4C. Using of fine-grained powders and application of pressure, which can be applied at hot pressing, during sintering process enables decreasing of sintering temperature too. [1, 4, 11-14].

Several metals (Al, Hf, Ti), non-metals (B, C) oxides (Al_2O_3, HfO_2, TiO_2, ZrO_2), and non-oxides (Si_3N_4, TiC, W_2B_5) are appropriate sintering additives for in situ sintering of B_4C based ceramic composites [8-10, 12, 13]. At the sintering of B_4C powder with titanium dioxide additive (TiO_2), the oxidic additive reacts with B_4C and form the titanium diboride (TiB_2), which become a part of phase composition of created composite material. The process of in situ boride creation significantly enhances of B_4C sinterability [9, 12, 14-16]. From thermodynamic presumption stems that B_4C- TiB_2 ceramic composite material is created in

consequence of in situ reaction between B_4C and TiO_2 initial powders, but the volatile species such as CO and CO_2 are a part of in situ reaction, too. The final phase composition of sintered samples changes with portion of TiO_2 in the initial powder mixture. The portion of volatile species grows with increased ratio of TiO_2 in the initial B_4C-TiO_2 powder mixture. Formation of volatile components complicates sample preparation. Increased care is necessary to give to their removing because removing of volatile species affect the densification of ceramic and so the rest-porosity of sintered samples [4, 8, 10, 17].

Microstructure and properties of B_4C-TiB_2 ceramic composite materials depend mainly on volume portion of created phases, densification, and grain size. The proper densification of every ceramic composite with the relative density near full density is a necessary condition for advanced properties of ceramic samples. The fracture toughness of B_4C-TiB_2 composite increases with portion of TiB_2 phase in consequence of better fracture of TiB_2 phase compared to B_4C phase. The hardness decreases with portion of TiB_2 phase because of lower hardness of TiB_2 phase compared to B_4C phase [4, 9, 15, 18].

Hot pressing process is one of preferred processes at the densification of B_4C based ceramics, because simultaneous application of temperature and pressure enables significant decreasing of sintering temperature compared to pressureless sintering [4, 10, 13, 15, 19]. Proper outgassing of B_4C based ceramic composite materials is important at hot pressing process with in situ reaction. Although hot pressing of B_4C based ceramics has been studied in several works and essential information about the final sintering temperature have been published, the information about heating stage of sintering process and application of pressure is less presented. An optimal sintering regime is necessary for both proper removing of volatile species during sintering and preparation of dense compacts with enhanced properties and it was the aim of this study with concentration of heating stage of hot pressing.

2 Used materials and evaluation methods

Hot pressing process was chosen for fabrication of B_4C-TiB_2 ceramic composite materials from B_4C and TiO_2 initial powders with the purity of 99 % and a particle size from 2 to 3 μm. Initial powder mixture contained 40 wt.% of TiO_2 sintering additive, because this composition was optimised in work [17]. The B_4C and TiO_2 initial powder mixture with 1 wt.% of binding wax was milled in Teflon container with B_4C mill balls and isobutyl alcohol lubricant for 4 hours in the horizontal mill. After drying of initial powder mixture, precursors of cylindrical shape with a diameter of 12 mm were prepared by die pressing in simple steel tool with floating die. The precursors were consequently hot pressed in graphite die with floating matrix of cylindrical shape with a diameter of 12 mm. Several hot pressing regimes with different heating stages of sintering processes were applied. However, the final process parameters such as sintering temperature of 1850 °C, pressure of 35 MPa, sintering time of 60 min and a vacuum atmosphere about 20 Pa were the same for all regimes, because they allowed optimal combination of mechanical properties according the result in work [17].

The surfaces of bulk samples were observed using stereomicroscope Zeiss Technival 2. The densities of hot pressed samples were measured using Archimedes method. Theoretical density of B_4C-TiB_2 (3.11 $g.cm^{-3}$) ceramic composite was calculated based on both theoretical densities of B_4C (2.52 $g.cm^{-3}$) and TiB_2 (4.52 $g.cm^{-3}$) phases and their volume portions (70.5 vol.% B_4C 29.5 vol.% TiB_2) measured using the image analysis for samples hot pressed at optimal sintering regime. Relative densities of B_4C-TiB_2 ceramic composites hot pressed at different sintering regimes were calculated by comparison of their densities with the theoretical density value of 3.11 $g.cm^{-3}$ (100 %). The microstructures were studied on cross sections of ceramic composite samples using light microscopy with Axiovert 40 MAT microscope and using electron microscopy with JEOL JSM-IT300 scanning electron microscope. The phase analysis was done using X ray diffraction method with Philips PW 1710 diffractometer. Volume portions of identified phases were measured using image analysis. The hardness and fracture toughness were measured by indentation method using Vickers indenter Buehler IndentaMet 1100.

3 Results and discussion

Sintering regime of boron carbide based ceramic composite material was optimised to enable removing of volatile species created by in situ reaction and microstructure formation during hot pressing of powder mixtures with the initial composition of B_4C with 40 wt.% TiO sintering additives. Although different sintering regimes were applied, the same final sintering temperature of 1850 °C, pressure of 35 MPa, time pressing time of 60 min in vacuum atmosphere about 20 Pa were applied for all composite samples.

Optimization of sintering regime during hot pressing of B_4C based ceramic composites

The optimization of sintering regime was focused on both heating stage of sintering process and application of pressure considering in situ reaction. The optimal sintering regime should enable to remove the volatile species which accompanied in situ reaction and prepare the ceramic composites without the rest porosity. The in situ reaction kinetic during hot pressing of B_4C and TiO_2 initial powder mixtures was identified by measuring of vacuum level in chamber of hot

press using vacuum gauge because the in situ reaction was accompanied by decrease of vacuum level. The W5Rh-W26Rh thermocouple was used for the measuring of sintering temperature. The densification progress during sintering of ceramic composite samples was observed according to motion of punch of die tool during hot pressing process and it allowed to calculate the densification speed in different sintering phases.

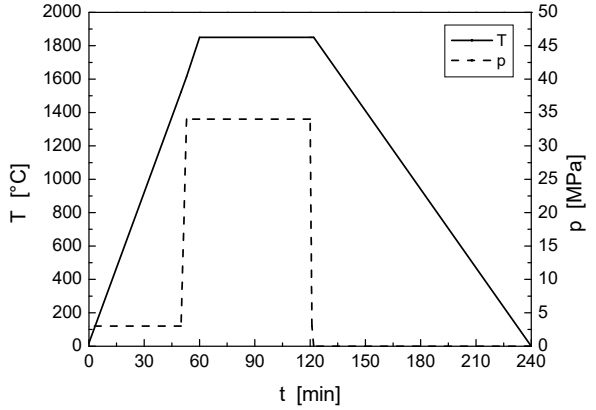

Fig. 1 *Progress of sintering temperature (T) and pressure (p) during initial sintering regime*

The initial sintering regime applied during the hot pressing of ceramic composite samples is demonstrated in fig. 1. Hot pressing in accordance with this initial sintering regime (fig. 1) was characterised by progressive application of sintering pressure after reaching the temperature of 1500 °C. In this stage of hot pressing, the vacuum level rapidly decreased, which indicated intensive in situ reaction between B_4C and TiO_2 initial powder components. Progress of sintering temperature and vacuum level during hot pressing of B_4C based ceramic composites is depicted in fig. 2. According to the vacuum level in fig. 2, volatile species significantly created in the temperature interval from 1500 to 1850 °C. Creation of relative high portion of volatile species, probably CO and CO_2, was confirmed by measuring of weight loss of hot pressed samples, which was about 30 wt.%. The maximal sintering pressure of 35 MPa was applied at the temperature about 1570 °C. The densification speed reached the maximal value of 2.5 $mm.min^{-1}$ shortly after application of full pressure of 35 MPa at the temperature of 1570 °C. Later, densification speed decreased and at the end of the dwell at the final sintering temperature of 1850 °C for 60 min it stabilised at the value of 0.01 $mm.min^{-1}$. At this stage of sintering process, the vacuum level in chamber of hot press chamber reached the minimal value about 20 Pa.

It was not possible to obtain ceramic composite compacts without surface defects using the initial sintering regime during hot pressing of ceramic composite samples. Application of pressure at the beginning stage of in situ reaction at the temperature of 1570 °C caused creation of several cracks and large pores. These defects can be seen on the base of the cylindrical surface of B_4C based ceramic composite compact in fig 3. It could be considered that the porosity of ceramic composite fulfilled the function of canals for removing of volatile species (CO and CO_2) created by in situ reaction during hot pressing process. The cracks were the consequence of premature application of pressure. The density values of these samples were 91.18 ± 1.22 % and are presented in fig. 6. Several surface defects caused relatively large scattering of measured density values as can be seen in fig. 6. As these values are not enough for reaching of advanced mechanical properties of sintered ceramic composite compacts, mechanical properties of samples were not measured.

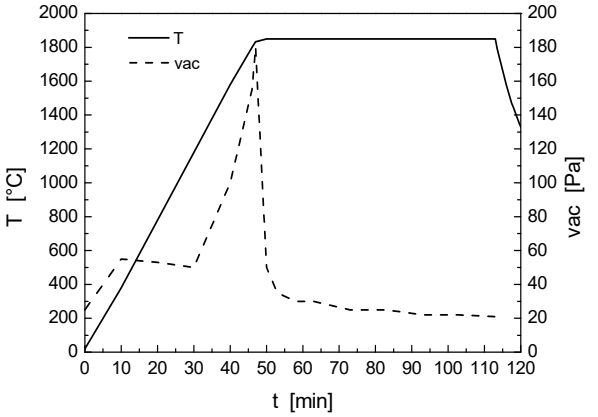

Fig. 2 *Progress of sintering temperature (T) and vacuum level (vac) during hot pressing of B_4C based ceramic composites*

Based on the results achieved during the hot pressing with the initial sintering regime in fig. 1, the heating stage of hot pressing process was several times modified. Significant progress in densification of hot pressed B_4C based ceramic composite materials was achieved by adding of a dwell at the temperature of 1570 °C for time of 60 min during the heating stage of a modified sintering regime. The dwell was added to prolongate the stage during removal of created volatile species during the densification of sample when the material has still adequate open porosity. The modified sintering regime had a positive effect on decreasing of cracks on surface of samples, but the densification of samples was insufficient. The density reached the value of 96.24 ± 0.32 %. When comparing the densities achieved at modified sintering regime with the initial regime (see fig. 6), significant increase of density with narrowed interval was achieved. However, the differences in the density values across the samples were observed on cross section of samples hot pressed with this modified sintering regime. Although the surfaces of samples were properly densified, the centres of samples proved relatively large

amount of rest porosity. The rest porosity in the centres of samples was caused by premature densification of surface areas of samples, before the volatile species could be removed from the bulk volume.

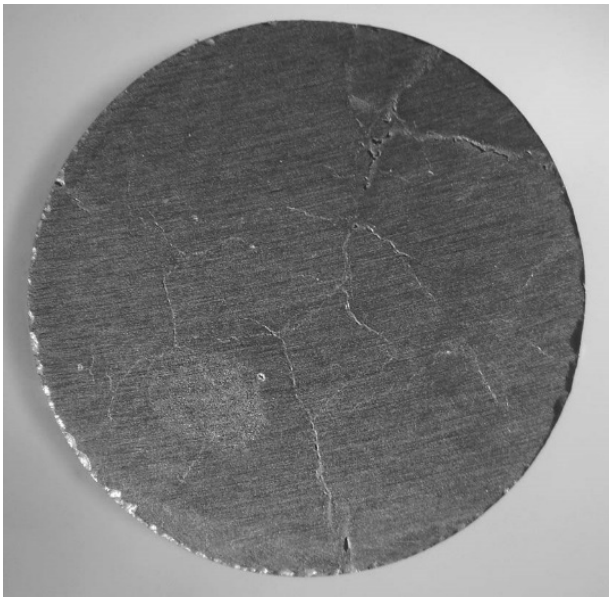

Fig. 3 *Surface cracks and pores created in B_4C based ceramic composite hot pressed using initial sintering regime*

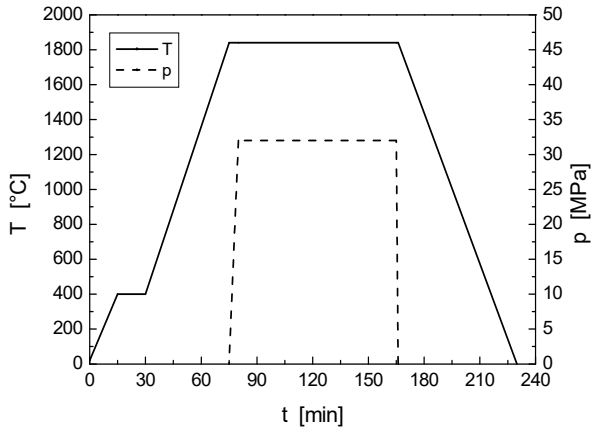

Fig. 4 *Progress of sintering temperature (T) and pressure (p) during optimal sintering regime*

Based on the results achieved during hot pressing using several modified sintering regimes, it was found that the full sintering pressure should be applied at higher temperature compared to previous regimes. So, the hot pressing process was modified as can be seen in fig. 4 and this regime could be labelled as the optimal sintering regime. During the heating stage of the optimal sintering regime a dwell at the temperature of 400 °C for time of 15 min was added to improve the removing of binding wax added at cold pressing of precursors. Progressive application of pressure started only at the maximal sintering temperature of 1850 °C. The optimal sintering regime allowed both the elimination of cracks and proper densification of ceramic composite samples with the density of 99.31 ± 0.26 %. The densities achieved at the optimal sintering regime are compared with densities measured at initial and modified sintering regimes in fig. 6. The average density at the optimal regime (99.31 %) increased significantly compared to modified regime (96.24 %), but variation of measured densities improved only slightly. Hot pressed bulk compacts were without any surface defects, as can be seen in fig. 5, where the cylindrical ceramic composite sample with a diameter of 12 mm and a height of 12 mm is documented.

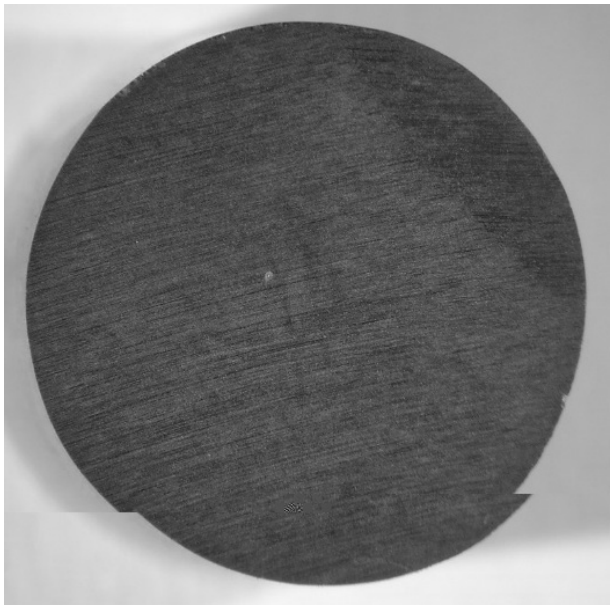

Fig. 5 *B_4C based ceramic composite without surface defects hot pressed using optimal sintering regime*

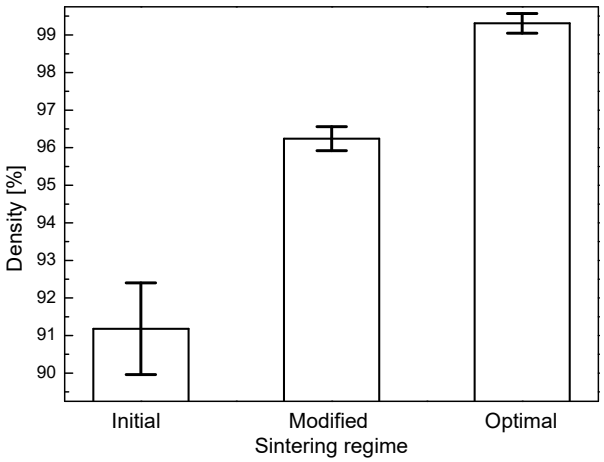

Fig. 6 *Comparison of densities at different sintering regimes*

Microstructure of B_4C-TiB_2 ceramic composites

The microstructures of B_4C based ceramic composites hot pressed at the same final sintering temperature of 1850 °C, the same sintering time of 60 min, and the same pressure of 35 MPa, but at applying of different sintering regimes are documented in fig. 7 (modified sintering regime) and 8 (optimal sintering regime). The microstructures of both presented samples consist of two phases which identification was

confirmed by XRD analysis. Dark areas in both micrographs represent boron carbide (B_4C) phases and light areas represent titanium diboride (TiB_2) phases. Without these phases, the sample in fig. 7, prepared using modified sintering regime, and with the average density of 96.24 % shows relatively large portion of rest porosity. Because of relatively low relative density values of hot pressed B_4C-TiB_2 ceramic composite depicted in fig. 7, mechanical properties of the composite were not measured.

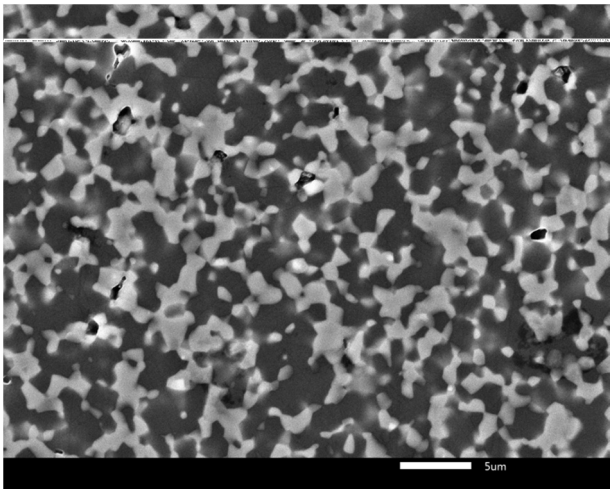

Fig. 7 *Microstructure of B_4C-TiB_2 ceramic composite hot pressed using modified sintering regime*

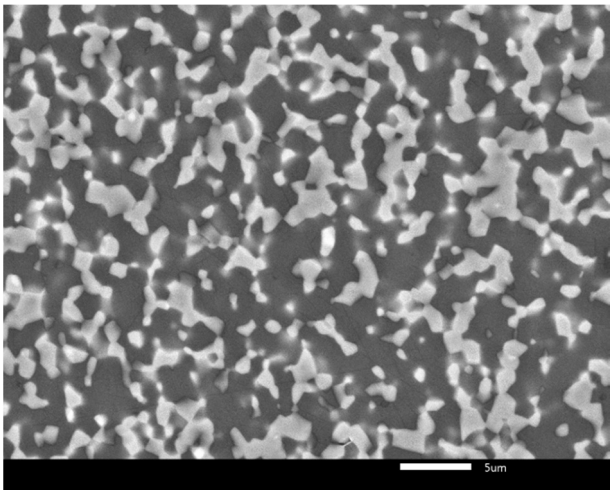

Fig. 8 *Microstructure of B_4C-TiB_2 ceramic composite hot pressed using optimal sintering regime*

Applying of the optimal sintering regime during hot pressing process of B_4C-TiB_2 ceramic composites enabled to prepare ceramic composite samples with the average density of 99.31 %. The microstructure of this B_4C-TiB_2 ceramic composite without visible rest porosity is depicted in fig. 8. The portions of in situ created phases in fig. 8 were measured using the image analysis. According the image analyse the microstructure of ceramic composite in fig. 8 consists of 70.5 vol.% B_4C matrix reinforced with 29.5 vol.% TiB_2 secondary phase. Fully dense microstructure was the consequence of advanced mechanical properties and the B_4C-TiB_2 ceramic composite reached the average hardness value of 29.8 GPa and the average fracture toughness of 6.9 MPa.m$^{1/2}$. These values can be compared with the results in works [2, 4, 8, 10, 11], where similar mechanical properties were measured.

4 Conclusions

Boron carbide based ceramic composite materials were hot pressed utilising in situ reaction of B_4C powder with 40 wt.% of TiO_2 sintering additive. The in situ reaction during hot pressing of B_4C and TiO_2 initial powder mixture resulted in creation of ceramic composite composed of B_4C matrix reinforced with TiB_2 secondary phase. In situ sintering of the composite was accompanied with evolution of volatile species, which must be properly removed during hot pressing process.

Based on the measurement of vacuum level during hot pressing process intensive volatile species were produced in the temperature interval from 1500 to 1850 °C. Creation of volatile species by in situ reaction caused large problems during hot pressing process. Cracks on the sample surfaces and significant porosity were observed at applying of pressure in sintering temperature interval from 1500 to 1570 °C. The porosity acted as canals for removing of volatile species.

Prolongated dwell of 60 min at temperature of 1570 °C decreased cracks amount on the surfaces of samples, but the densification of samples was insufficient. The samples reached the density value of 96.24 ± 0.32 %. The porosity in the centres of samples was caused by premature densification of surface areas of samples, before the volatile species could be removed from the bulk volume.

The optimal sintering regime enabled to prepare fully dense B_4C-TiB_2 ceramic composite materials. Firstly, the precursors were heated to the sintering temperature of 1850 °C, and secondly, pressure of 35 MPa was progressively applied. This sequence was necessary for achieving of ceramic composite compacts without any surface defects. The ceramic composite hot pressed at optimal sintering regime were composed of B_4C matrix with 29.5 vol.% TiB_2 secondary phase. The composites reached the density of 99.31 ± 0.26 %, average hardness value of 29.8 GPa, and fracture toughness of 6.9 MPa.m$^{1/2}$.

Acknowledgements

This work was supported by the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic under the VEGA 1/0298/18 contract. The work was supported by UVP STU Bratislava the ITMS 26240220084 project.

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