Thermal conductivity and thermal shock resistance of TiB₂-based UHTCs enhanced by graphite platelets

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Abstract

TiB₂-SiC-C and TiB₂-TiC-C heteromodulus ceramics were sintered by reactive hot pressing of TiC-B₄C-Si and TiC-B₄C precursors at 1830 °C and 30MPa. Sintering time at the maximum temperature was between 2 and 8 min. The reactions in TiC-B₄C-Si green body create submicron (100 – 400nm) TiB₂ crystals inside silicon carbide grains as well as B_xSi_yC_z nanofibers, which nucleate near SiC surfaces. Low hardness graphite platelets are formed within the hard matrix during the in-situ exothermic reaction. “Soft-hard” grain combination produces substantially improved fracture toughness (up to 9MPa·m^{1/2}). The materials also demonstrate high thermal conductivity (up to 120W/m·K) and high thermal shock resistance. The thermal shock crack growth is arrested by the graphite platelets.

Key words: reactive sintering; thermal shock resistance; thermal conductivity; toughness; crack resistance, heteromodulus ceramics; titanium diboride; silicon carbide.

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Introduction

Titanium diboride belongs to a family of ultra-high temperature ceramics (UHTC). The material possesses unique combination of physical and mechanical properties which secures its use in many applications. For instance, the diboride-based ceramics play a crucial role in aerospace industry being able to survive extreme heating of aerofoil wing leading edges, nosecones, engine cowl inlets, etc. [1, 2, 3, 4, 5, 6]. Titanium boride ceramics have outstanding mechanical characteristics and are more stable in contact with iron than WC, BN, and Si₃N₄. This provides the ground to use them in metal cutting tools [7], [8]. Furthermore, there is widening field of applications in fuel saving automotive engines [9], energy production, including solar energy harvesting [10, 11, 12]. The major issue hampering the utilization of monolithic UHTCs in all application areas is low thermal shock resistance (TSR). During inevitable temperature variations this leads to the material fracture [3].

According to Lu and Fleck [13] there are two possible criteria of thermal shock material failure: if maximum local tensile stress exceeds the tensile strength (σ_f) of the solid, and if maximum stress intensity factor for the pre-existing crack exceeds the fracture toughness (K_{1C}) of the solid. The corresponding thermal shock resistance limits can be estimated [13, 14] as:

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

and

$$R'' = \frac{K_{1C}(1-\nu)k}{\alpha E}, \quad (2)$$

where ν , α , k , and E are the Poisson's ratio, thermal expansion coefficient, thermal conductivity and Young's modulus respectively. As was shown in [13] the fracture toughness criterion (2) is more restrictive for brittle materials than the strength one (1).

Low toughness, e.g. crack resistance, is common disadvantage of single-phase monolithic ceramics and for titanium diboride single phase material the corresponding value approximates at around 4 – 5 MPa·m^{1/2} [7, 5]. Second phase addition can substantially improve the resistance. The introduction of silicon carbide into TiB₂-matrix resulted in the material toughening to: 5.76 MPa·m^{1/2} [15]; 6.6 MPa·m^{1/2} [16]; 6.8 MPa·m^{1/2} [17, 18] and 7.34 MPa·m^{1/2} [19]. The titanium carbide addition allows even better K_{1C} improvement to: 7.43 MPa·m^{1/2} [20] and 8.4 MPa·m^{1/2} [21].

Conventional hot pressing of near non-porous TiB₂-SiC composites requires 120 min at 1850 °C and 20MPa [15, 17] or 60 min at 1900 °C and 30MPa [22]. Wang *et al* [20] manufactured dense TiB₂-40wt.%TiC ceramics in two stage pressureless process: 240 min of sintering at 1500 °C followed by 60 min at 2000 °C. Bhaumik *et al* [23] obtained TiB₂-15wt.%TiC with less than 1% porosity by high-pressure (3GPa) sintering at 2500 °C for 5 min. Spark-plasma sintering allowed densification of TiB₂-20vol.%SiC material at 1900 °C and 30 MPa for 10 min [24].

In order to moderate the sintering process parameters of TiB₂-TiC and TiB₂-SiC UHTCs without the addition of phases with low melting temperature, the reactive sintering techniques based on high temperature interaction between boron carbide and titanium have been developed [16, 25, 21]. The green body of composition 3Ti + B₄C resulted in 2TiB₂ + TiC composition when hot pressed at 1600 °C and 41 MPa for 240 min [25] and at 1800 °C and 35 MPa for 60 min [21]. The sintered materials, nevertheless, were not fully densified containing 8% and 3% of pores correspondingly. Zhao *et al* investigated sintering of green bodies 2Ti + B₄C + Si [26] and 2Ti + B₄C + Si + xTiB₂ [16] at 1700 °C and 32 MPa for 30 min. In those cases, the ceramic composition corresponds to the right side of the following general equation:

(x = 0; 0.3; 1.3; 3.2).

This process successfully used the advantages of the exothermic reaction in 2Ti + B₄C + Si stoichiometric mixture. But it was noted that for lower x the resulted materials had lower densities. For instance, TiB₂-SiC ceramics with silicon carbide content exceeding 15 vol.% had more than 3% of pores.

Different precursor mixture of 2TiC-B₄C-3Si has been used by Zhang *et al* [18, 19] to produce 2TiB₂-3SiC composition. The disadvantage however was that applying the pressure after the reaction completion only resulted in the dense ceramics after pressing at 1900 °C and 30 MPa for 30 min.

It can be seen that for high TSR (criteria (1) and (2)) the material thermal conductivity and fracture toughness should be raised while Young's modulus should be lowered. Young's modulus reduction with no negative impact on the material high-temperature properties can be achieved in so called heteromodulus ceramics (HMC). This type of material presents a combination of high-E matrix with low-E graphite or graphite-like boron nitride inclusions [2, 27]. The comparison of TiB₂ and graphite properties (Tab. 1) shows that the soft graphite phase introduction can not only essentially reduce Young's modulus but also rise thermal conductivity. Both effects will present an advantage for ceramic thermal shock resistance.

Table 1. TiB₂ and graphite properties [28, 29, 30]

<i>Property</i>	<i>TiB₂</i>	<i>Graphite</i>
Young's modulus E, GPa	560	20
Thermal conductivity k, W/m·K	60-120	400
Coefficient of thermal expansion α, 10 ⁻⁶ K ⁻¹	7.4	1*
Hardness H _V , GPa	30	0.3
Crack resistance K _{IC} , MPa·m ^{1/2}	6.2	1

*The mean value at 600°C [30]

Some of the first HMCs have been presented by Hasselman *et al* [31] who had demonstrated that TSR of alumina and zirconium carbide can be substantially improved with the addition of 30 vol.% of h-BN. Similar results for TiB₂-AlN-BN and TiC-C composites were demonstrated by Bannister and Swain [32] and by Shabalin *et al* [2] respectively. The problem of the mentioned HMCs is their comparatively low crack resistance, which for TiB₂-based materials [32] did not exceed 4 MPa·m^{1/2}.

As it has been shown in our previous works [33, 34], graphite can be produced inside the ceramic matrix during in-situ reactions between titanium and boron carbides. In this case, the mixed grain composition provides fracture toughness improvement, as the graphite inclusions in form of submicron platelets can stop crack propagation [35]. The presented work is the further investigation of the influence of reactively created graphite on mechanical parameters and thermal shock resistance of brittle matrixes in order to improve the performance of TiB₂-based UHTCs.

2. Experimental procedure

Commercially available powders of TiC (~70 µm), B₄C (~20 µm), and Si (~20 µm), from Donetsk Reactive Factory, Ukraine, were used as a green body materials for the TiB₂-TiC-C and TiB₂-SiC-C composites. The materials purity, as stated by the manufacturers, was at around 99.0 at%.

The green body compositions were chosen to comply with the stoichiometry of the following reactions:

when: $x = 2, 4, 8, 16, 34$ (samples 1 - 5) and $y = 0.5, 1, 1.5, 2.5$ (samples 6 - 9). The compositions of the green bodies are presented in Table 2.

Table 2. The composition and sintering parameters of the samples

Sample powders		Initial		Sintering parameters			Sintered compositions estimated according to (4) and (5)			
№	TiC, at. %	B ₄ C, at. %	Si, at. %	T, °C	P, MPa	t, min	TiB ₂ , vol. %	TiC, vol. %	SiC, vol. %	C, vol. %
1	93.2	6.8	-	2000	30	8	7.1	89.2	-	3.7
2	86.5	13.5	-	1950	30	4	14.3	78.3	-	7.4
3	76.2	23.8	-	1900	30	4	25.8	60.7	-	13.5
4	61.5	38.5	-	1860	30	4	43.3	34	-	22.7
5	44.4	55.6	-	1830	30	4	65.6	-	-	34.4
6	34.8	43.5	21.7	1830	30	2	47.9	-	48	4.1
7	38.1	47.6	14.3	1830	30	4	53.6	-	32.3	14.1
8	40	50	10	1830	30	4	57.2	-	22.9	19.9
9	42.1	52.6	5.3	1830	30	4	61	-	12.2	26.7

The majority of fully densified samples were produced in vacuum by hot pressing at 1830 °C and 30MPa. The graphite die was heated with AC (50 Hz) within a hot-pressing system DCS-1 produced by SRC Synthesis (Kiev, Ukraine) and the University of Huddersfield. The heating rate (after preheating at 500 °C for 20 min) was approximately 100 °C/min. The sintering system allows to apply constant pressure (monitored by the load cell) to the sintered sample and to monitor sample densification during sintering. The densification is observed as sample shrinkage (sample thickness reduction) during the hot pressing. The sintered specimens were in the form of 10 mm discs. The initial charge (green body) amount has been calculated to satisfy compositions of reactions (4) and (5) right-hand side in a such a way that the thickness of the fully densified sample was at around 4 mm. The time point of the synthesis termination (heating halt) was chosen for each sample individually. The time point was based on the condition of non-progressive densification (e.g. end of material shrinkage). For the presented compositions, the duration of the material sintering at the highest temperature ranged between 2 and 8 min (See Tab.2).

The bulk density of the sintered ceramics was measured by the Archimede's method. The theoretical densities (ρ_{th}) were estimated from the rule of mixtures. The material densities were assessed in line with right-hand side of the reactions (4) and (5). The following densities of the individual phases were used: $\rho(\text{SiC}) = 3.21 \text{ g/cm}^3$, $\rho(\text{TiB}_2) = 4.51 \text{ g/cm}^3$, $\rho(\text{TiC}) = 4.93 \text{ g/cm}^3$, $\rho(\text{C}) = 2.26 \text{ g/cm}^3$, $\rho(\text{B}_4\text{C}) = 2.51 \text{ g/cm}^3$. The crystalline phases were identified by X-Ray Diffraction (XRD) and supported by the EDX analysis. Grain morphological structure was assessed by Scanning Electron Microscopy (SEM). Samples were cleaved for the SEM analysis. This allowed to avoid polishing artefacts in the ceramic with significant hardness variations.

Vickers hardness measurements were performed with a load of 49 N and 10 s holding at the load. The measurements were done on the 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 [36].

Fig. 1. Graphic representation of Therm-1 system in: thermal conductivity (a) and thermal shock (b) configuration modes

Thermal conductivity analysis was performed by means of the direct heat flux measurements through a sample at the controlled temperature gradient by utilisation of Therm-

1 equipment produced by SRC Synthesis (Kiev, Ukraine) (See Fig. 1a). The material thermal conductivity was calculated according to the universal formula:

$$k = \frac{Qx}{tA\Delta T} \quad (6)$$

where Q – the heat flux through the area A of the sample with the thickness x during time t at the temperature difference $\Delta T = \Delta T_{th.c.} - \Delta T_{con.}$. The $\Delta T_{th.c.}$ is directly measured temperature difference between thermocouples at the sample sides. $\Delta T_{con.}$ is the contact temperature drop. This temperature drop increases linearly with applied power (heat output Q/t) and has been evaluated by means of the heat flux measurements for different well-known materials (Al, Cu, TiB₂, TiC, SiO₂ in our case) with tabulated conductivity. The contacts between thermocouple discs and the sample were improved with the thermo-conductive paste “Thermal Grizzly Kryonaut” with the thermal conductivity of 12.5W/m·K. The error of thermal conductivity measurements increases with k value and was experimentally estimated to be below 12% for k = 150W/m·K.

Thermal shock crack growth was examined according to the indentation-quench method, as described in [37]. The disk specimens were polished and indented using a Vickers pyramidal indenter with a load of 49 N and 10 s holding time. Five indentations were made on each specimen. Four cracks at the pyramid ribs are formed after each indentation. This way 20 cracks per sample were measured. The samples were heated to a preselected set of temperatures: 200, 300, 400, 500, 600, and 700°C. The heating was done in air for 10 min and then quenched into a water bath at room temperature (20 °C). The quenching series were performed in the Therm-1 system with the modified base (see Fig. 1b), when the thermostat was replaced with water filled vessel. Samples were heated in the top heater and then dropped into the water. The radial crack lengths of each indentation were measured before and after each quenching event by an optical microscope. The crack growth was expressed as percentage to the initial crack length as:

$$(c_i - c_0)/c_0 \times 100\% \quad (7)$$

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

The heat effect and adiabatic temperature were calculated using thermochemistry data from the NIST Chemistry WebBook [38].

3. Experimental results and discussion

3.1. Densification kinetics and composite structure

The XRD analysis of samples ## 6 – 9 (Fig.2) showed that no initial phase (TiC, B₄C, or Si) remained in the material after the synthesis while indicating TiB₂, SiC, and graphite. As green body composition changes, so does the concentration of produced phases - with silicon carbide content decreasing and graphite increasing from samples #6 to #9. That confirms the phase compositions of the created materials to be as the ones predicted on the basis of reaction (5). The *in-situ* phase transformation of the samples ##1 – 5 proceeds according to the reaction (4), which has been already shown earlier [35]. Therefore, sintered sample compositions correspond to those presented in Table 2.

Fig. 2. XRD spectra for samples ## 6 – 9

The material consolidation during synthesis varied considerably and was predominantly affected by the initial green body composition. The densification speed was lowest for sample 1 and increasing gradually to sample 5 (See Fig. 3a, 3b). Silicon presence in 2TiC-B₄C system (samples 6 - 9) resulted in an improvement of the green body consolidation process which ultimately allowed to obtain non-porous material at 1830°C pressed for 2 min. Considerable densification in silicon presence started at lower, as compared to silicon-free samples, temperature and occurred via two clear stages at 1200 – 1400°C and at 1600 – 1800°C (Fig. 3c, 3d). The latter is in an agreement with the previous results presented in [39], when the powder mixture with the same composition as the 6-th sample was sintered at the similar parameters in vacuum.

Fig. 3. The sample thickness (a, c) and the charge compression speed (b, d) dependences.

As it was previously shown [33], the sintering kinetics and processes depend on the green body composition and chemical reactions. The densification mechanism in the case of TiC-B₄C into TiB₂-C transformation is as following. At high enough temperatures boron atoms sublime from B₄C and condense onto TiC grain surfaces [40]. The surface chemical reaction leads to formation of TiB₂ plate-like nuclei. The new phase grows and resides inside titanium carbide grain [41]. Boron carbide, after losing almost all boron transforms into carbon-based sponge. The graphite sponge mechanical properties are inferior even compared to a dense graphite. Formation of titanium diboride crystals inside a TiC particle results in development of considerable tensile stress and eventual cleavage of the parental crystal. As the reaction occurs near the free grain surface, the cleaved TiB₂ fragments fill the intergranular pore and provide additional densification.

The reaction between titanium and boron carbides ($2\text{TiC} + \text{B}_4\text{C} = 2\text{TiB}_2 + 3\text{C}$; $\Delta H = -129\text{kJ/mol}$) is exothermic. This may lead to the local heating up to adiabatic temperature (See Tab. 3). The value of adiabatic temperature increment depends on the green body composition. The elevated temperature promotes all the thermo-activated processes and further intensify material consolidation. According to the reaction (4), the final composition of samples 1 – 5 consisted of: (i) reactively formed TiB₂ and graphite particles; (ii) some TiC grains, which survived the sintering process due to the excess of the TiC phase in the initial powder mixtures. Therefore, the consolidation is intensified by the higher B₄C content as the composite reactively sintered fraction rises. Sample 1, having only 10% of the sintered fraction did not reach theoretical density even after 8 min at 2000°C (See Tab. 3).

In our previous work [35], when we undertook hot pressing of TiC-B₄C compositions similar to samples 2 – 5, the isothermal dwelling time was 16 minutes. However, as it can be seen from the densification kinetics (See Fig. 3a, 3b), most of the green bodies had ceased shrinking considerably earlier. Therefore, to prevent the unnecessary grain coarsening we terminated the sintering process soon after the consolidation stopped. For most of the compositions, the corresponding time was around 4 min (See Tab. 2).

Table 3. Theoretical densities of non-porous initial (ρ_{nit}) and product (ρ_{prod}) compositions, the experimental values for the sintered samples, and the adiabatic temperature of in-situ reactions

Sample #	ρ_{init} , g/cm ³	ρ_{prod} , g/cm ³	$\frac{\rho_{\text{init}} - \rho_{\text{prod}}}{\rho_{\text{init}}}$, %	ρ_{exp} , g/cm ³	$\rho_{\text{exp}}/\rho_{\text{prod}}$, %	T_{ad} , °C
1	4.78	4.77	0.2	4.56	96	2060
2	4.66	4.64	0.4	4.6	99	2080
3	4.46	4.42	0.9	4.66	105	2160
4	4.16	4.09	1.7	4.38	107	2260
5	3.77	3.68	2.4	3.82	104	2440
6	3.21	3.76	-17.1	3.7	98	2730
7	3.37	3.73	-10.7	3.87	104	2670
8	3.47	3.72	-7.2	3.92	105	2610
9	3.61	3.69	-2.2	3.9	106	2540

Silicon introduction influences the densification and structure formation by two additional processes. The first one is an intermediate liquid phase which is produced at approximately 1400°C due to Si melting. Then, there is higher overall reaction enthalpy in silicon presence ($2\text{TiC} + \text{B}_4\text{C} + 3\text{Si} = 2\text{TiB}_2 + 3\text{SiC}$; $\Delta H = -336\text{kJ/mol}$). The resulting higher adiabatic temperature accompanying by the intermediate liquid should promote both, reaction itself and material consolidation, due to intergrain slippage and improved atomic transport (e.g. diffusion). At the same time, there is a negative dilatometry of the reaction (5) which origins from the product density being 20.1% higher than that of the initial composition (See Tab.3). In oppose, the reaction (4) has a positive dilatometry of 2.4%.

The mentioned mechanisms lead to higher overall shrinkage of TiC-B₄C-Si samples. However, the *in situ* reaction in this case might have ambiguous influence on the final material density: it intensifies consolidation because of the charge mobility improvement, but may lead to formation of the additional porosity because of the negative dilatometry [42]. This probably explains why the 6-th sample has the greatest difference in the densities of the initial and product compositions and is most porous from the set.

Composite structure of TiB₂-TiC-C reactively pressed system has been discussed earlier [33]. The structure is a mixture of TiB₂-TiC super hard matrix with soft graphite inclusions of two different types: sponge-like volumes of 2-5 μm in diameter (remnants of boron depleted

B₄C grains) and submicron platelets emerging as a result of TiC into TiB₂ transformation (See Fig. 4).

Fig. 4. SEM images of sample 5 in (a) back-scattered electrons with TiB₂ grains (light) and graphite inclusions (dark) and (b) secondary electrons; graphite plates can be seen on the magnified region

Fig. 5. Electron images of sample 6 (a) and sample 9 (b) (back-scattering electron detector, Z-contrast mode); light grey – TiB₂, grey – SiC, dark grey – graphite

It is possible to expect that the grain size distribution of $\text{TiB}_2\text{-SiC-C}$ samples should be similar to $\text{TiB}_2\text{-C}$ (sample 5, Fig. 4) with graphite inclusions (remnants of B_4C grains) partially transformed into SiC particles. However, there are several features showing the different structure formation process in $\text{TiB}_2\text{-SiC-C}$. Firstly, the characteristic grain size of sample 6, with the highest fraction of silicon carbide, is approximately 7 μm for SiC and 5 μm for TiB_2 (Fig. 5a). While titanium diboride grains are similar to those in the sample 5, the silicon carbide ones are essentially bigger than the “parental” graphite inclusions. Reduction of silicon concentration in the green body leads to sintered composite structure refinement and in the 9-th sample most of TiB_2 particles do not exceed 2 μm and SiC ones are in general between 2 and 4 μm (See Fig. 5b). The tendency is even more interesting considering the fact that the 9-th sample with finer grains had isothermal dwelling time at the highest temperature twice as long as the 6-th one (See Tab. 2). This shows that the formed silicon carbide and graphite particles during synthesis (samples 8, 9) somehow suppresses growth of nucleated TiB_2 and SiC crystals.

It should be noted that comparatively large silicon carbide grains are not monolithic and have submicron (100 – 400nm) TiB_2 particles inside (see Fig. 6). Similar particles were also observed inside the graphite areas remaining after B_4C decomposition during $\text{TiC-B}_4\text{C}$ interaction [41]. As is shown in [39], both silicon carbide and titanium diboride appear in $\text{TiC-B}_4\text{C-Si}$ powder mixture at temperatures below 1200°C. It should be noted that this is 200 °C below silicon melting point. Therefore, the reactions in the green body start in solid phases. Silicon bond carbon extracted from TiC crystals as well as the one released during boron carbide decomposition. At higher temperature boron can be observed sublimating from boron carbide [33] and creating B-vacancies. This in turn allow Ti atoms diffusion into the decomposing B_4C grains. The latter gradually transform into the predominantly C-based foam. Titanium impregnation creates some TiB_2 inside the foam [41]. As silicon melts, the interaction with carbon intensifies and the process of SiC formation approaches its conclusion.

Fig. 6. Back-scattering electron image of submicron TiB_2 particles (bright spots near the centre of the image) inside the SiC grains.

Fig. 7. Sample #6 fracture surface with $B_xSi_yC_z$ nanofibers at SiC grain surfaces: Everhart-Thornley detector (ETD), secondary electrons (a) and back-scattering electron detector, Z-contrast mode (b)

Apart from already mentioned TiB_2 submicron particles, there is one more type of objects visible during the SEM analysis of the sample #6. It is possible to see nanofibers which are attached to SiC grains (Fig. 7). Careful EDX analysis of the nanofiber bunch shows that main elements are boron, silicon and carbon in the proportion at around 4:2:1. Considering the actual sizes of the electron beam scattering and penetration depth, titanium lines in the EDX spectrum are most probably produced by the nearby TiB_2 grain. Moreover, as the fibres are imbedded in SiC grains, Si and C concentration in the fibre bunch EDX results should be overestimated. It leaves us with boron-based $\text{B}_x\text{Si}_y\text{C}_z$ nanotubes which grow during the reactive sintering process. The existence of such compound has been predicted by Samsonov et al [43]. Mechanical characteristics of $\text{B}_{11}\text{CSi}_2$ compound were calculated by Ann and Goddard [44]. Finally, $\text{B}_x\text{Si}_y\text{C}_z$ crystals formed after boron carbide dissolving in silicon melt were recently reported by Yurkov et al [45]. We do not think that the existence of $\text{B}_x\text{Si}_y\text{C}_z$ nanofibers in the manufactured composites affects mechanical properties considerably. Nevertheless, the very possibility of such structure formation at presented reactive sintering conditions can be the special topic for the future investigations.

3.2. Mechanical and thermal properties

The mechanical and thermal properties of the samples are summarised in the Table 4. As it can be seen, the material toughness (e.g. crack resistance) depends predominantly on graphite content, increasing up to $9\text{MPa}\cdot\text{m}^{1/2}$ at 10-20 vol.% of the soft graphite phase. The results correlate with those presented in [35], where such toughness improvement was explained with the crack tip blunting on the graphite inclusions. The correlation confirmed the adequacy of 4 min isothermal dwelling applied in the current work to sufficiently consolidate the TiC- B_4C compositions. It should be noted, that even at carbon content of 30% the toughness does not drop below $5\text{MPa}\cdot\text{m}^{1/2}$. Relatively low hardness of samples ## 1 and 2 (See Tab. 4) can possibly be caused by the rather excessive porosity.

It should be also noted that fracture toughness of TiB_2 -SiC-C materials (samples ## 6 - 9) exceeds the corresponding values of TiB_2 -SiC-CNT composites [39] showing that at the

current sintering conditions the graphite platelets (See Fig. 4) are more efficient crack propagation obstacles than carbon nanotubes.

The thermal conductivity of TiC-TiB₂-C composites (Samples 1 - 5) increases with graphite content from 35W/mK to 120W/mK. As is shown in [29], the graphite thermal conductivity is around 400 W/mK while the thermal conductivity of TiC and TiB₂ averages at around 30 W/mK [46] and 65 W/mK [28] respectively. Optimisation the graphite content is of paramount importance for the composite heat flow and crack resistance. The thermal conductivity of all the TiB₂-SiC-C samples is very close and resided in 120-130 W/mK region. The reason for this is probably in the fact that the silicon carbide, which partially replaces graphite, has the thermal conductivity between 100 and 250 W/mK [47] itself. The total content of graphite and SiC phases in the samples ##6 – 9 varies between 40 and 50 vol.% and this provides for the lightly abstracted high heat flow the heterogeneous material.

Table 4. Mechanical and thermal properties of the sintered composites

Sample #	SiC, vol.%	C, vol.%	H _v , GPa	K _{IC} , MPa·m ^{1/2}	k, W/m·K	E*, GPa	R''**, W/m ^{1/2}
1	0	3.7	14.2	6.5±0.7	35±1	503	48
2	0	7.4	13	9.4±1	45±3	486	97
3	0	13.5	16.4	8.9±0.9	58±3	458	134
4	0	22.7	12.2	8.8±1.2	75±7	415	207
5	0	34.4	6.6	5±0.5	120±5	361	231
6	48	4.1	25.6	6.2±1	115±10	471	208
7	32.3	14.1	18.7	7.6±0.8	130±13	434	310
8	22.9	19.9	14.4	8.4±0.7	120±13	414	326
9	12.2	26.7	11	8±0.7	130±13	388	349

* Calculated with the rule of mixtures basing on the product phase characteristics

** Calculated with the equation (2)

The R'' parameter has been calculated according to the equation (2) with the use of the experimental data for thermal conductivity and fracture toughness.

The Young's modulus and the thermal expansion coefficient were estimated according to the rule of mixtures for the final compositions (See Tab. 2) with the following parameters for

the components: $E(\text{SiC}) = 410 \text{ GPa}$, $\alpha(\text{SiC}) = 2 \cdot 10^{-6} \text{ 1/K}$ [48]; $E(\text{TiB}_2) = 565 \text{ GPa}$, $\alpha(\text{TiB}_2) = 7.4 \cdot 10^{-6} \text{ 1/K}$ [28]; $E(\text{TiC}) = 520 \text{ GPa}$, $\alpha(\text{TiC}) = 2 \cdot 10^{-6} \text{ 1/K}$ [2]; $E(\text{graphite}) = 20 \text{ GPa}$, $\alpha(\text{graphite}) = 1 \cdot 10^{-6} \text{ 1/K}$ [29].

It can be seen from Tab.4, that R'' parameter rises initially monotonically with the graphite content for $\text{TiB}_2\text{-TiC-C}$ system while it has maximum at approximately 25 vol.% for $\text{TiB}_2\text{-SiC-C}$ composites. The $\text{TiB}_2\text{-SiC-C}$ composites also show higher values of thermal shock resistance.

Fig. 8. The average percentage growth of indentation cracks versus quenching temperature difference (ΔT) for ceramics with different graphite volume content in $\text{TiB}_2\text{-TiC-C}$ (a) and $\text{TiB}_2\text{-SiC-C}$ (b) systems

The results of the indentation-quench experiments are presented on Fig. 8 and correlate with the theoretically estimated R'' parameter. Cracks in $\text{TiB}_2\text{-TiC-C}$ ceramics with low graphite content start to grow noticeably at quenching events just above $100 \text{ }^\circ\text{C}$ and destroy the samples completely at quenching from temperatures above $300 \text{ }^\circ\text{C}$. The increase in graphite content to 12% allows to up the material thermal shock resistance. Further graphite addition improved it substantially and the sample with 22% was not destroyed even after quenching from 700°C . The $\text{TiB}_2\text{-SiC-C}$ system behaves broadly similarly to the $\text{TiB}_2\text{-TiC-C}$, but SiC presence further stabilises the system.

To extract the material thermal shock resistance value from the experimental data presented on Fig. 8, an approximate 50% quenching temperature ($\Delta T_{0.5}$) was deduced. The temperature is defined as one at which the average crack growth adds 50% to the initial crack value. The comparison of the latter with R'' parameter (See Fig. 9a and Fig. 9b) allowed to make some conclusions about the thermal shock resistance of the manufactured hetero-modulus ceramics. Firstly, the soft graphite phase undoubtedly impedes the heat shock crack growth. At the low (up to 15 vol.%) graphite content the $\Delta T_{0.5}$ and R' values show similar tendencies for both systems indicating the R' parameter to be an adequate reflection of the material performance at fast temperature variations. Secondly, the matrix having higher thermal conductivity ($\text{TiB}_2\text{-SiC}$) is shown to be more stable than the one with the lower conductivity ($\text{TiB}_2\text{-TiC}$). Further soft phase addition, however, nullified the differences between the two systems and resulted in the resistance to the thermal shock crack growth being dependent on the graphite content mostly. Higher graphite concentrations up to around 30 vol.% improves the thermal shock resistance

Fig. 9. The thermal shock resistance (R'') parameter estimated according to equation (1) with the use of the experimental data for the sintered composites (a) and the quenching temperature ($\Delta T_{0.5}$) resulted in crack length increasing by 50% (b)

The resent modelling provided by Li et al [14] showed that the TSR of ultra-high-temperature ceramics can be substantially improved by means of the microcracks introduction. In the sintered systems the soft graphite platelets can easily play a role in development of such

microcracks. At higher graphite concentration platelet inclusions become an additional advantage for the composite thermal shock resistance rise and should be considered while estimating the material performance.

4. Conclusions

A reactive sintering approach for $\text{TiB}_2\text{-SiC-C}$ ceramics manufacturing has been developed starting from $\text{TiC-B}_4\text{C-Si}$ green bodies. In-situ exothermal reactions allowed full densification to be achieved by hot pressing at 1830°C and 30 MPa for 2 - 4 min. The exothermic nature of reactions and presence of graphite and SiC created dense heteromodulus ceramic with high crack and thermal shock resistance. There is also $\text{B}_x\text{Si}_y\text{C}_z$ nanotube growth near SiC grain surfaces during the material consolidation.

Thermal shock resistance of the sintered materials increases substantially at high graphite content. This growth is provided by simultaneous rise of thermal conductivity and fracture toughness and decrease of Young's modulus. The best results can be observed for the samples with 20 – 30 vol.% of the soft graphite phase.

The developed reactive sintering approach to thermal shock resistance improvement by the incorporation of graphite platelets inside the superhard refractory material can possibly be applied to produce ultra-high temperature materials based on other $\text{MeB}_2\text{-SiC}$ UHTCs (Me = Zr, Hf).

The created $\text{TiB}_2\text{-SiC-C}$ and $\text{TiB}_2\text{-TiC-C}$ heteromodulus ceramics are considerably more mechanical and thermal shock resistant than the corresponding pure, single phase, refractory materials.

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