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Effect of TEG on Oxidation of TiC–ZrC Equimolar Blend at Mechanical Alloying

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A detailed x-ray diffraction study of TiC–ZrC equimolar blend at mechanical alloying in a planetary ball mill is provided. An essential oxidation of carbide components is established. As found, Oxygen from the charge and reaction zone of the mill promotes gradual decomposition of ZrC with the formation of cubic c-ZrO₂, which further transforms into its monoclinic modification m-ZrO₂. TiC accumulates the Oxygen in tetrahedral voids of its crystal lattice, forming Ti_xCO_y oxycarbide. Addition of 3% vol. TEG powder to the initial TiC–ZrC charge completely inhibits the oxidation.

Key words: mechanical alloying, thermoexfoliated graphite, carbide, crystal structure, x-ray diffraction.

Проведено детальне рентгеноструктурне дослідження продуктів механо-хімічного оброблення в планетарному млині двох еквімолярних сумішей TiC–ZrC та TiC–ZrC + 3% об. ТРГ, в результаті якого показано, що карбідні компоненти еквімолярної TiC–ZrC суміші виявляють схильність до їх суттєвого окиснення. При цьому наявний в шихті та реакційній зоні млина кисень сприяє поступовому розпаду карбіду цирконію ZrC з утворенням стабілізованої вуглецем кубічної модифікації оксиду цирконію c-ZrO₂, яка з часом трансформується в його моноклінну модифікацію m-ZrO₂, а карбід TiC накопичує Оксиген в тетраедричних порах його кристалічної ґратниці з утворенням оксикарбіду Ti_xCO_y. Додаток 3% об. порошку терморозширеного графіту (ТРГ) до вихідної суміші TiC–ZrC повністю перешкоджає процесу окиснення кожного з карбідів, а механохімічна активація сумішей

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викликає вибивання атомів металу (скоріше, йонів Ti^{4+} та Zr^{4+}) до реакційної зони млина з утворенням структурних дефектів в ґратницях карбідів, що створює передумови для подальшого формування взаємних твердих розчинів заміщення $Zr_{1-x}Ti_xC$. Одержана в роботі МХ активована дрібнодисперсна (розмір кристалітів до 20 нм) суміш $TiC-ZrC + 3\%$ об. ТРГ може бути рекомендована як ефективний наповнювач для створення консолідованих нанокристалічних керамік на базі TiB_2 та інших боридів.

Ключові слова: механохемічний синтез, терморозширений графіт, карбід, кристалічна структура, рентгенівська дифракція.

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1. INTRODUCTION

TiB_2-TiC and TiB_2-ZrC ceramic composite materials are known to have high hardness, good wear resistance, high fracture toughness and corrosion resistance [1–5]. However, since it is very difficult to compact these materials by conventional sintering, to synthesize TiB_2-TiC and TiB_2-ZrC composites the method of reaction sintering of powder charge of B_4C , pure Ti and Zr metals at temperatures above $1500^\circ C$ is applied.

Problems related to complicated compaction of ceramics at direct sintering of TiB_2 and TiC powders were eliminated by applying mechanical treatment of the initial charge in a high-energy planetary mill at the first technological stage. As a result of such processing for 30 hours the crystallite size of phase components decreased to 15 nm and the composite sintered at $1500-2100^\circ C$ from the processed powder demonstrated quite good characteristics [6].

High mechanical properties of TiB_2-TiC composite materials (relative density is above 98%, hardness of 94.7 HRA, tensile strength of 487–776 MPa, fracture toughness is up to $7 MPa \cdot m^{1/2}$ [7]) and TiB_2-ZrC [5], as well as the possibility of their direct synthesis from ultrafine powders of components [6] prompted us to provide mechanical processing of equimolar mixture of $TiC-ZrC$ carbides. Milled charge will be used as precursor for further synthesis of $TiB_2-TiC-ZrC$ ceramic nanocomposite material.

2. MATERIALS AND METHODS

The charge of raw carbide powders (Table 1) was sealed in ZrO_2 vial and subjected to cyclic processing (10 min of processing and 2 min of cooling) in BM 6 Pro planetary ball mill. Eleven ZrO_2 balls (15 mm in diameter) were used for the processing of the charge; the mass ratio of the balls to powder was 10:1. During experiment the temperature of the

TABLE 1. Materials studied.

Experiment	TiC (CBC grade, 99.9% wt. purity)		ZrC ('Y' grade, 99.9% wt. purity)		Thermoexfoliated graphite (TEG)	
	% wt.	% vol.	% wt.	% vol.	% wt.	% vol.
1	36.7	43.9	63.3	56.1	–	–
2	36.7	43.9	63.3	56.1	3.7	3.0

working area in the reaction zone did not exceed 70°C, the rotation speed of the vial was 500 rpm.

Phase transformations taking place at mechanical alloying have been studied by x-ray diffraction methods on the test samples selected after each complete hour of milling. XRD data was collected with DRON-3M automatic diffractometers (CuK α radiation) in a discrete mode under the following scanning parameters: observation range $2\theta = (20-100)^\circ$, step scan was 0.05° and counting time per step was 3 s. Sample was rotating in the plane of the cuvette attachment during measurements. The original software package [8], including full complex of standard Rietveld procedures, has been used for analysis and interpretation of the x-ray diffraction patterns obtained, namely, determination of both peak positions and integral intensities of the Bragg reflections by means of full profile analysis; carrying out qualitative and quantitative phase analysis using PDF data for phase identification and the least square method for lattice parameters refinement; testing of the structure models and refining crystal structure parameters (including coordinates of atoms, atomic position filling, texture, *etc.*); calculation of the parameters of the real structure of the individual phases (coherent block sizes and lattice strain values).

3. EXPERIMENTAL RESULTS

3.1. Experiment 1. Mechanical Alloying of TiC–ZrC Equimolar Blend

The results of x-ray phase analysis indicate that with increasing of milling time, the phase composition of the equimolar blend studied gradually changes. Therefore, the presence of the c-ZrO $_2$ cubic oxide phase was detected on diffraction patterns of 2 hours milled test samples, in addition to the phases of the charge components (Fig. 1). Besides, the quantity of this phase is gradually increasing with milling time increasing. Advanced phase analysis (Table 2) has revealed that the apparent balance of phase content is somewhat disturbed, namely, the weight ratio of phases containing Titanium (TiC) and Zirconium (ZrC and c-ZrO $_2$) does not correspond to the charge composition. A detailed study of the

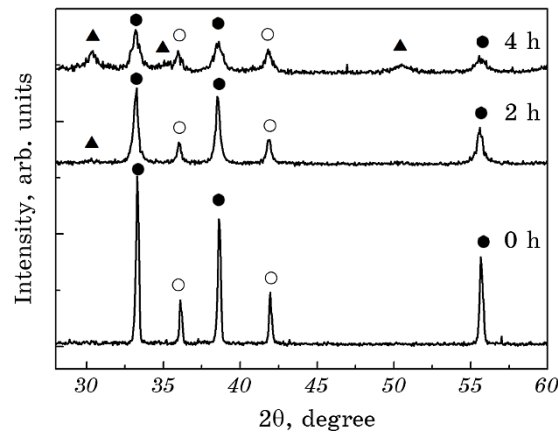


Fig. 1. Diffraction patterns of test samples of mechanically alloyed TiC–ZrC equimolar blend. Phases are marked as: ●—ZrC; ○—TiC, ▲—c-ZrO₂.

final test sample (4 h of milling) has revealed that it contains the low-temperature monoclinic modification of zirconium oxide m-ZrO₂ in addition to the mentioned TiC, ZrC and c-ZrO₂ phases. Taking this into consideration, the quantitative phase content becomes completely balanced (Table 2).

According to the data of Ref. [9], at certain conditions the oxygen atoms presented in charge can diffuse into ZrC grains with the formation of a layer of carbon-stabilized c-ZrO₂ phase. In our experiment, the lattice parameter of the milled charge is $a = 0.5125(2)$ nm. As the oxidation process develops, c-ZrO₂ transforms into its monoclinic modification m-ZrO₂, which exists in a fine crystal state. It is this process that takes place at oxidation of ZrC carbide during mechanical alloying of TiC–ZrC blend. Herein, the presence of x-ray amorphous m-ZrO₂ phase in milled samples causes a certain discrepancy in the quantitative content of the test samples studied (Table 2).

The lattice parameters of both carbides are changed with processing time increasing (Fig. 2). To clarify the nature of these changes we provided a detailed x-ray diffraction study of the crystal structure of ZrC and TiC phases milled.

It is known that in the crystal structure of monocarbides of stoichiometric composition (NaCl type) atoms of metal components (Zirconium or Titanium) and Carbon are arranged in the regular systems of points of $Fm\bar{3}m$ space group as follows: four atoms of Ti or Zr are placed in $4(a) 0 0 0$; four atoms of C are placed in $4(b) 0.5 0.5 0.5$. Therefore, the occupation density of $4(a)$ position by metal atoms was refined in the first turn and possible arrangement of Oxygen atoms at formation of Zirconium or Titanium oxycarbides was simulated. As a result, it was obtained that the imperfection of the crystal lattice of carbides gradually increases with

TABLE 2. Phase composition of mechanically alloyed blends.

Mill- ing time t , h,	Experiment 1. TiC–ZrC			Experiment 2. TiC–ZrC + 3% vol. TEG		
	Phase compo- sition ¹⁾	Lattice parameter a , nm		Phase com- position ¹⁾	Lattice parameter a , nm	
		ZrC	TiC		ZrC	TiC
0	ZrC (63) + + TiC (37)	0.46826(4)	0.43262(3)	ZrC (63) + + TiC (37) + + C _{gr}	0.46826(4)	0.43262(3)
1	ZrC (63) + + TiC (37)	0.46814(6)	0.43246(9)	ZrC (63) + + TiC (37)	0,4682(1)	0,4324(1)
2	ZrC (59) + + TiC (39) + + c-ZrO ₂ (1) + + m-ZrO ₂ (?)	0.46830(9)	0.43259(2)	ZrC (63) + + TiC (37)	0,4683(1)	0,4325(1)
3	ZrC (51) + + TiC (45) + c- ZrO ₂ (4) + m- + ZrO ₂ (?)	0.4682(2)	0.4328(1)	ZrC (62) + + TiC (38)	0,4682(2)	0,4326(2)
4	ZrC (39) + TiC (51) + c-ZrO ₂ (10) + m-ZrO ₂ (?) ²⁾	0.4681(1)	0.4331(4)	ZrC (60) + + TiC (39) + + c-ZrO ₂ (1) ³⁾	0,4681(1)	0,4327(1)

¹⁾ Phase composition on % vol.

²⁾ Quantitative balance for all present phases: ZrC (32) + TiC (40) + c-ZrO₂ (12) + m-ZrO₂ (16).

³⁾ Vial debris.

processing time, and the Oxygen presented in these lattices partially fills the tetrahedral voids of 8(c) 0.25 0.25 0.25 position. Accuracy of the calculations was controlled by the reliability factor R_B , which usually did not exceed 0.03 (Table 3). Figure 3 gives solid evidence of the decrease of metal component in the crystal lattices of carbides.

Analysis of the parameters of the real structure of carbides by the approximation method on (111) and (222) reflections (TiC and ZrC powders were used as standards) have shown that fine crystal state with the crystallite size D of about 30 nm is formed in test samples after 1 hour of milling. As milling time increases, the crystallite size of ZrC carbide continues to decrease down to 13 nm, while D_{TiC} is not changed (Table 4). There is no lattice strain (ϵ) in ZrC carbide milled, but its value changes slightly for TiC phase. Dislocation density ρ increases with processing time increasing for both carbides. It should be noted that it was impossible to define the parameters of TiC real structure in some cases due to

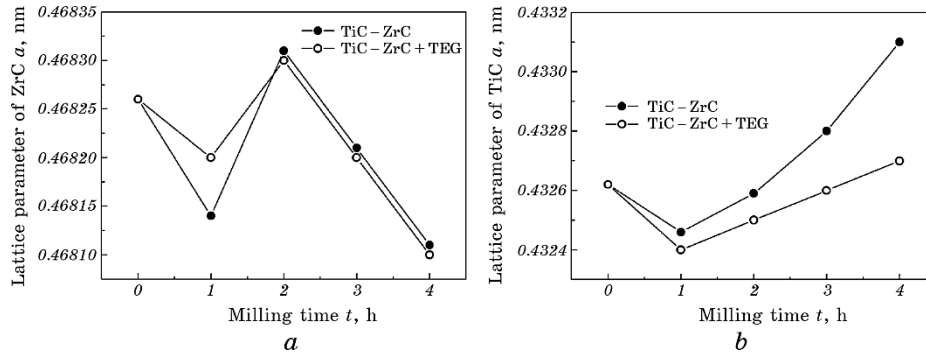


Fig. 2. Dependences of lattice parameters of ZrC (a) and TiC (b) on milling time.

the significant broadening of the diffraction peaks. Calculated parameters of the real structure of carbides milled are listed in Table 4 and presented in Fig. 4.

Thus, mechanical alloying of the TiC-ZrC equimolar blend is accompanied by an essential oxidation of charge. In subsequent experiment

TABLE 3. Crystal structure refinement for mechanically alloyed ZrC and TiC.

Mill- ing time t , h	Experiment 1. TiC-ZrC					Experiment 2. TiC-ZrC + 3% vol. TEG				
	Compound	Phase con- tent, at. %			R_B	Com- pound	Phase con- tent, at. %			R_B
		Zr	C	O			Zr	C	O	
0	ZrC	50	50	-	0.018	ZrC	50	50	-	0.022
1	Zr _{0.89} C	47	53	-	0.026	Zr _{0.96} C	49	51	-	0.020
2	Zr _{0.82} C	45	55	-	0.029	Zr _{0.89} C	47	53	-	0.018
3	Zr _{0.78} CO _{0.04}	43	55	2	0.029	Zr _{0.82} C	45	55	-	0.034
4	Zr _{0.69} CO _{0.07}	41	59	4	0.031	Zr _{0.75} C	43	57	-	0.031
Mill- ing time t , h	Experiment 1. TiC-ZrC					Experiment 2. TiC-ZrC + 3% vol. TEG				
	Compound	Phase con- tent, at. %			R_B	Com- pound	Phase con- tent, at. %			R_B
		Ti	C	O			Ti	C	O	
0	TiC	50	50	-	0.018	TiC	50	50	-	0.016
1	Ti _{0.92} C	48	52	-	0.026	Ti _{0.88} C	47	53	-	0.021
2	Ti _{0.78} C	44	56	-	0.029	Ti _{0.82} C	45	55	-	0.013
3	Ti _{0.75} CO _{0.13}	40	53	7	0.029	Ti _{0.85} C	46	54	-	0.024
4	Ti _{0.67} CO _{0.42}	32	48	20	0.016	Ti _{0.92} C	48	52	-	0.015

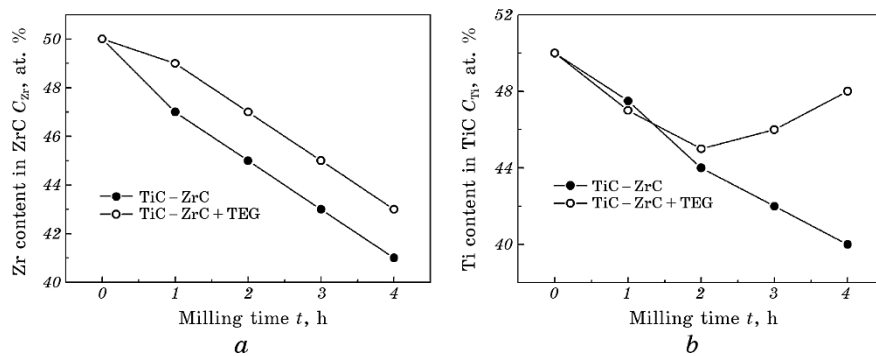


Fig. 3. Dependences of Zirconium (*a*) and Titanium (*b*) content in the metal lattice of ZrC and TiC on milling time.

3% vol. of thermoexfoliated graphite (TEG) was added to the initial charge in order to suppress oxidation.

3.2. Experiment 2. Mechanical Alloying of TiC–ZrC Equimolar Blend with Addition of 3% vol. TEG

Diffraction patterns of the test samples do not contain any additional phases (Fig. 5, Table 2). Dependences of the crystal lattice parameters of TiC and ZrC carbides on processing time are like those for charge milled without TEG (Fig. 2, Table 2). However, lattice parameters of TiC phase are slightly smaller.

Refinement of the crystal structure of TiC and ZrC carbides milled has revealed the absence of dissolved Oxygen and the decrease in filling of their metal sublattices by Titanium or Zirconium atoms (Table 3, Fig. 3). Besides, this value gradually decreases with the processing time for

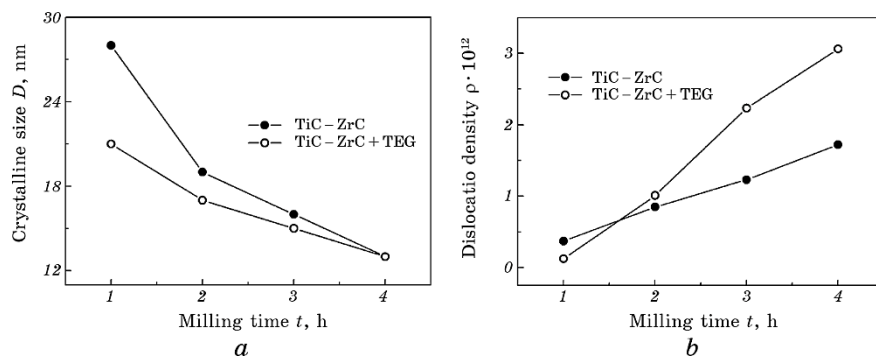


Fig. 4. Dependences of the crystallites size (*a*) and the density of dislocations (*b*) of ZrC carbide on milling time.

TABLE 4. Parameters of the real structure of mechanically alloyed ZrC and TiC.

Milling time <i>t</i> , h	Experiment 1. TiC–ZrC			Experiment 2. TiC–ZrC + 3% vol. TEG		
	Crystal- lite size <i>D</i> , nm	Lattice strain ε , %	Dislocation density ρ , E+12	Crystal- lite size <i>D</i> , nm	Lattice strain ε , %	Dislocation density ρ , E+12
ZrC						
0	>150	–	–	>150	–	–
1	28(4)	0.0	0.372(5)	21(3)	0.29(2)	0.154(6)
2	19(3)	0.0	0.849(4)	17(1)	0.31(2)	1.010(5)
3	16(1)	0.0	1.230(5)	15(2)	0.46(2)	2.230(8)
4	13(2)	0.0	1.720(7)	13(2)	0.52(4)	3.060(8)
TiC						
0	>150	–	–	>150	–	–
1	30(4)	0,08(1)	0.291(4)	19(2)	0.16(3)	0.557(6)
2	30(4)	0.30(2)	1,040(7)	19(9)	0.00	0.556(6)
3	24(2)	0.21(2)	?	20(3)	0.00	0.693(7)
4	?	?	?	20(3)	0.11(2)	0.758(7)

ZrC carbide, while for TiC phase it begins to increase after passing a certain minimum (Fig. 3).

Calculation of the real structure parameters of carbide phases shows that the nature of changes in the crystallite size and dislocations density of for both charges milled is the same (Fig. 4). However, ZrC crystal lattice just accumulates the internal stresses in the presence of TEG and isn't decomposed with the formation of oxycarbide phase (Table 4).

In general, the experiment on mechanical alloying of equimolar TiC–ZrC blend undoubtedly shows that the addition of 3% vol. of carbon in the form of TEG to the initial charge leads to complete inhibition of the oxidation.

4. DISCUSSION

Study of the kinetics of transformations of the carbide components of equimolar TiC–ZrC blend shows the tendency to oxidation of the powders milled (Table 2). Moreover, the oxidation of charge components is carried out in different ways. Oxygen presented in the charge and reaction zone of the mill promotes the gradual decomposition of ZrC with the formation of c-ZrO₂ carbon-stabilized cubic modification of zirconium oxide, which further transforms into its monoclinic modification m-ZrO₂. Generally, the transformation of ZrC takes place as:

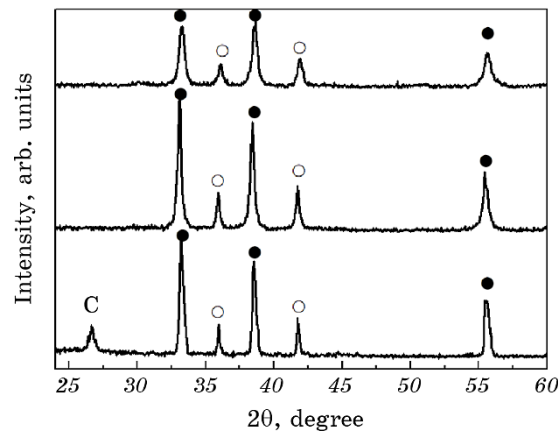
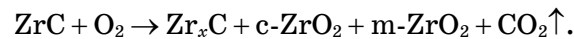
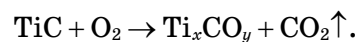


Fig. 5. Diffraction patterns of test samples of mechanically alloyed TiC–ZrC + 3% vol. TEG equimolar blend. Phases are marked as: ●—ZrC, ○—TiC, C—Graphite.



There is almost no solubility of Oxygen in the ZrC crystal lattice at mechanical alloying in contrast to the significant solubility of Oxygen in the tetrahedral voids of TiC lattice. Thus, the oxidation of TiC titanium carbide occurs according to the scheme:



Addition of about 3% vol. TEG powder to the initial TiC–ZrC equimolar blend completely inhibits the oxidation of the carbides. But the metal sublattices of both carbides are gradually depleted by Titanium or Zirconium atoms at mechanical alloying of both mixtures studied (TiC–ZrC and TiC–ZrC + TEG) (Table 3). At this, the clusters of these atoms, more properly, Ti^{4+} and Zr^{4+} ions, are saturated the reaction zone of planetary mill. This process dominates at the beginning of mechanical alloying (up to 1 hour of processing) and is accompanied by a decrease in the lattice parameters of both carbides (Fig. 2).

The dynamics of further changes in the parameters of TiC and ZrC crystal lattices in dependence on the existing structural defects is quite interesting (Fig. 6).

The obtained dependences (Fig. 6) could be explained only by assuming the existence of dissolution of Zirconium atoms/ions in TiC lattice, which leads to an increase in its lattice parameter and a supposed decrease in the degree of structural defect. In return, Titanium at-

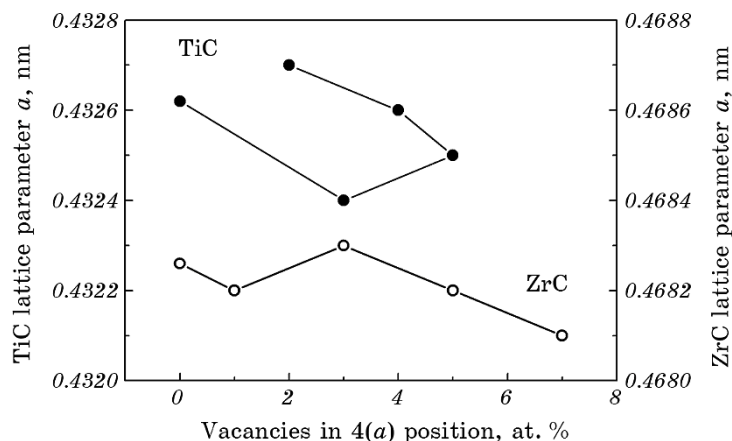


Fig. 6. Dependences of TiC and ZrC lattice parameters on the structural defects induced at processing of TiC-ZrC + TEG charge.

oms/ions dissolution in ZrC lattice results in a decrease in its lattice parameter and a supposed increase in the degree of defect of the structure. That is, the preconditions for formation of mutual $Zr_{1-x}Ti_xC$ substitutional solid solutions are created at mechanical alloying. Previously, such solid solutions were obtained from a mixture of TiC-ZrC by the method of spark plasma sintering (SPS) [10–13]. B. C. Ocak *et al.* [14] have studied the effect of graphene nanoparticles (GNP) dopants on TiC-ZrC ceramics obtained by SPS. It was shown that the highly dense (relative density is over 99%) ZrC-TiC-GNP composites are formed at sintering of the initial charge with addition of 3% vol. GNP. The phase composition of these composites is formed by $Zr_{1-x}Ti_xC$ substitutional solid solutions of [14].

In this work it was shown that the addition of 3% vol. TEG to ZrC-TiC powder blend completely prevents the oxidation of carbides at mechanical alloying. Moreover, the addition of 3% vol. Carbon is known to significantly improve the fracture toughness of TiB_2 -TiC ceramics due to the fact that graphite inclusions prevent the growth of cracks [15]. Thus, TEG dopants to ZrC-TiC charge may act in two ways, namely, they prevent the oxidation of a charge milled, and on the other hand, TEG dopants create preconditions for improving the mechanical properties of bulk composite material.

5. CONCLUSIONS

Detailed x-ray diffraction study of test samples of equimolar blends of TiC-ZrC and TiC-ZrC + 3% vol. TEG mechanically alloyed in a planetary mill under the same mode has revealed the following.

Carbide components of TiC–ZrC equimolar blend are significantly oxidized at processing. Oxygen present in the charge and reaction zone of the mill promotes the gradual decomposition of ZrC with the formation of carbon-stabilized cubic modification of zirconium oxide c-ZrO₂, which eventually transforms into its monoclinic modification m-ZrO₂, while TiC carbide accumulates the Oxygen atoms in tetrahedral voids of its crystal lattice, forming of Ti_xCO_y oxycarbide.

Addition of TEG (3% vol.) to the initial TiC–ZrC charge completely inhibits the oxidation.

Mechanical alloying causes an extraction of metal atoms (rather Ti⁴⁺ and Zr⁴⁺ ions) from charge to the reaction zone of mill with the formation of structural defects in ZrC and TiC crystal lattice, which creates preconditions for further formation of Zr_{1-x}Ti_xC solid solutions.

Fine-crystalline (crystallite size up to 20 nm) TiC–ZrC + 3% vol. TEG activated powder can be recommended as an effective filler for the creation of consolidated nanoceramics based on TiB₂ and other borides.

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