IMPROVING ENERGY EFFICIENCY OF SILICON CARBIDE CERAMICS PRODUCTION BY BATCH REGULATION

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Abstract: The article discusses an energy-efficient method for producing SiC-based composites via doping with oxide eutectic compositions and batch granulometry regulation. The influence of batch granulometry on physico-mechanical properties of ceramics is studied, and fractions ratio is determined allowing us to obtain a dense material with improved strength and fracture toughness. Such ceramics shows excellent mechanical behavior and holds much promise as a structural and armor material.

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Introduction

Silicon carbide is a non-oxide compound that exhibits excellent toughness, wear resistance, heat conductivity, refractoryness, strength, low thermal expansion coefficient, significant oxidation resistance up to 1500 °C, and chemical and corrosion resistance (Balkevich, 1984; Tretyakov, 1998; Matthews & Rawlings, 2004). Its density is 2,5 times lower than that of steel. These features make silicon carbide desirable as a structural material in IC-engines, gas turbines, cutting tools, and ceramic bearings. Strong chemical bond makes it possible to apply this material as light armor since most part of kinetic energy in a rapid mechanical interaction between a bullet and an armor element is expended in opening chemical bonds within the material. Another notable feature of silicon carbide is its relatively low cost.

Processing of silicon carbide invokes temperatures up to 2150 – 2200°C. Despite a wide range of applications for SiC-based ceramics, matters of energy and resource efficiency as well as constant demand for more reliable media stimulate a search for novelty materials with improved physico-mechanical properties and reduced sintering temperature. Thus, one of the possible solutions here involves doping SiC with eutectic sintering aids.

The purpose of this study was to suggest an energy-saving and easily-implemented technique for manufacturing dense silicon carbide ceramics with tailored properties.

Material and methods

The sample batch consisted primarily of silicon carbide powder with mean grain size of 3 – 4 μm. Mean particle size in silicon carbide nanopowder was 45 – 55 nm.

Candidate oxide eutectic systems for the present research included $CaO – Al_2O_3 – Y_2O_3$, $Al_2O_3 – ZrO_2$, and $MgO – Al_2O_3 – Y_2O_3$. Additives in $CaO – Al_2O_3 – Y_2O_3$ and $Al_2O_3 – ZrO_2$ systems were prepared using respective oxides, which were blended in desired proportions and calcined to complete possible physico-chemical transformations. In $MgO – Al_2O_3 – Y_2O_3$ system, alumomagnesian spinel and yttrium-aluminum garnet were prepared separately—the prior by calcining a mixture of salts, the latter by heterophase precipitation in water solutions of yttrium and aluminum chlorides.

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Pre-fabricated additives in CaO – Al_2O_3 – Y_2O_3 and MgO – Al_2O_3 – Y_2O_3 systems were mixed together with SiC powder in calculated proportions. The batch was prepared in a vibro-mill with PTFE chambers with alumina grinding media in acetone. Slurries were dried at room temperature and passed through a 05 (approx. 30 BSS mesh) sieve. A hot solution of paraffin in CCl_4 (5% wt.) was used as binder, whereas mineral component was added portionwise and heated till complete solvent evaporation. Samples of different shape (disks and blocks) were uniaxially cold-pressed at 100 MPa and fired at 1900°C in Argon with preliminary calcination at 700 °C in carborundum electric furnace in air.

Results and discussion

The resulting structural properties (i.e., density and porosity) and mechanical characteristics are presented in Table 1.

Table 1: Structural and mechanical properties of expermental samples (starting material – α-SiC)

Batch composition	Parameters		
	ρ, g/cm^3	**P_o, %**	**σ_{bend}, MPa**
SiC + 15 % wt. CaO – Al_2O_3 – Y_2O_3	2.56	38.0	70 ± 22
SiC + 20 % wt. CaO – Al_2O_3 – Y_2O_3	2.58	34.0	82 ± 24
SiC + 15 % wt. MgO – Al_2O_3 – Y_2O_3	2.60	34.0	100 ± 20
SiC + 20 % wt. MgO – Al_2O_3 – Y_2O_3	2.70	28.0	120 ± 22
SiC + 15 % wt. Al_2O_3 – ZrO_2	2.64	33.0	100 ± 24
SiC + 20 % wt. Al_2O_3 – ZrO_2	2.69	30.0	110 ± 20

Source: Authors

The increase of sample density correlated with additive content changing from 15 to 20 % wt. for CaO – Al_2O_3 – Y_2O_3, Al_2O_3 – ZrO_2, and MgO – Al_2O_3 – Y_2O_3 systems; however, this parameter was still below the value for undoped silicon carbide. The additive in MgO – Al_2O_3 – Y_2O_3, ceteris paribus, provided for a denser and less porous material. Mechanical strength and open porosity of ceramics with magnesia-based sintering aid were by an average 15 MPa higher and 5% lower, respectively, than those of ceramics with Ca-based additive or alumina-zirconia composition for the same additive content. Still, the obtained material displayed significant porosity and poor mechanical properties.

In order to improve mechanical characteristics of the developed material, the following hypothesis was provisionally accepted as a basis for further research. For general provisions for closest particle packing in bimodal distribution, Poluboyarinov & Rutman (1966) suggested that the desired particle size ratio should be 10:1. Assumed that coarse fraction was presented by α-SiC with mean particle size of 3 – 5 μm and fine fraction, by eutectic additive with mean particle size of 300 – 500 nm, the effect of fractions ratio on density was studied for samples pressed at 100 and 200 MPa. True densities of the additives were considerably different; hence, fractions ratio mentioned above was only applicable in terms of volume fractions. The content of fine fraction varied from 15 to 50% vol. in 5% increments. The resulting densities are shown in Table 2.

As the experimental data suggest, the densest materials were obtained at fraction ratio of 70:30, both for 100 and 200 MPa (Batch No. 3). Further study was carried out on compositions with 30% vol. of eutectic additives in CaO – Al_2O_3 – Y_2O_3, Al_2O_3 – ZrO_2, and MgO – Al_2O_3 – Y_2O_3 systems. Samples were pressed at 200 MPa and fired at 1900 °C in Argon. Experimental variables included open porosity, mean density, and bending strength (see Table 3).

Table 2: Compositions and properties of bimodal batch samples

Batch No.	Composition, % vol.		Pressure – 100 MPa		Pressure – 200 MPa	
	SiC 3-5 μm	Dopant 300-500 nm	ρ, g/cm^3	P_o, %	ρ, g/cm^3	P_o, %
$CaO – Al_2O_3 – Y_2O_3$ additive						
1	85	15	2.06	38.0	2.14	35.4
2	80	20	2.17	35.5	2.27	32.3
3	70	30	2.33	32.4	2.40	30.1
4	60	40	2.28	35.3	2.38	32.5
5	50	50	2.12	41.2	2.32	35.6
$MgO – Al_2O_3 – Y_2O_3$ additive						
1	85	15	2.13	37.2	2.22	34.4
2	80	20	2.25	34.8	2.35	31.8
3	70	30	2.44	31.6	2.52	29.5
4	60	40	2.43	34.1	2.52	31.6
5	50	50	2.30	39.7	2.53	33.8
$Al_2O_3 – ZrO_2$ additive						
1	85	15	2.21	36.1	2.30	33.6
2	80	20	2.33	34.2	2.48	30.2
3	70	30	2.59	30.4	2.65	28.7
4	60	40	2.57	34.1	2.68	31.1
5	50	50	2.51	38.4	2.71	33.3

Source: Authors

Consequently, the eutectic additive content of 30% vol. is not sufficient for considerable densification and strengthening of the material. Supposedly, silicon carbide in use was not active for sintering enough to obtain ceramics with improved mechanical properties; gaps between larger SiC grains were too wide to be healed during sintering.

Table 3: Structural and mechanical properties of samples with 30 % vol. of eutectic dopant (starting material – α-SiC)

Batch composition	Parameters		
	ρ, g/cm^3	P_o, %	σ_{bend}, MPa
$SiC + CaO – Al_2O_3 – Y_2O_3$	2.73	30.2	94 ± 22
$SiC + MgO – Al_2O_3 – Y_2O_3$	2.84	24.2	132 ± 26
$SiC + Al_2O_3 – ZrO_2$	3.07	26.3	126 ± 24

Source: Authors

Further tuning of ceramics properties was carried out on compositions with trimodal particle size distribution corresponding to the closest trimodal packing principle (particle size ratio – 100:10:1) (Poluboyarinov & Rutman, 1966). Coarse grain size comprising 3 – 5 μm, the finest fraction in such compositions should not exceed 30 – 50 nm. This finest fraction was presented by silicon carbide nanopowder with mean particle size of 45 – 55 nm. Intermediate fraction with mean particle size of

300 – 500 nm, same as above, was presented by eutectic additives, which would not only intensify sintering but also form the closest particle packing in shaping. Silicon carbide nanopowder and intermediate fraction content varied from 10 to 20 and from 25 to 35% vol., respectively, in 5% increments. The resulting structural characteristics are presented in Table 4.

As the experimental data suggest, density of trimodal batch samples was higher than that of the bimodal ones. The highest achieved densities corresponded to 20% vol. of silicon carbide nanopowder (n-SiC). If this value dropped to 10 – 15 %, a decrease in mean density and open porosity growth would occur.

With cost concerns in mind, the content of n-SiC was kept as low as possible, and further work was carried out on 15% vol. compositions (see Table 5).

It was observed that implying ultrafine dopant makes way for a dramatic increase in structural and mechanical characteristics. Ceteris paribus, regardless of the eutectics content materials with 15% vol. of n-SiC, exhibited greater strength and far lower open porosity compared to those for ceramics without nano-scale non-oxide constituent. Implementation of ultrafine additive seemingly modifies structure formation process on compacting stage, promotes sintering, and alters hardening mechanism, which results in increased mechanical strength of the composite material.

Still, ceramics with 15% vol. of n-SiC remained porous, and taking into account experimental data on density and porosity of trimodal batches (see Table 4), it proved necessary to keep the dopant content at 20 %, as shown in Table 5.

Table 4: Compositions and properties of trimodal batch samples

Batch No.	**Composition, % vol.**			**Pressure – 100 MPa**		**Pressure – 200 MPa**	
	SiC 3-5 μm	**Dopant 300-500 nm**	**n-SiC 45-55 nm**	**ρ, g/cm³**	**P_o, %**	**ρ, g/cm³**	**P_o, %**
$CaO – Al_2O_3 – Y_2O_3$ additive							
1	65	25	10	2.70	20.5	2.83	16.8
2	60	30	10	2.73	20.5	2.86	17.0
3	55	35	10	2.76	20.7	2.88	17.3
4	60	25	15	2.75	19.2	2.91	14.4
5	55	30	15	2.78	19.3	2.91	15.4
6	50	35	15	2.76	20.6	2.90	16.7
7	55	25	20	2.77	18.5	2.91	14.3
8	50	30	20	2.81	18.4	2.95	14.1
9	45	35	20	2.78	20.0	2.95	15.3
$MgO – Al_2O_3 – Y_2O_3$ additive							
1	65	25	10	2.81	20.0	2.93	16.4
2	60	30	10	2.85	20.1	2.97	16.8
3	55	35	10	2.87	20.9	3.01	17.0
4	60	25	15	2.84	18.9	3.01	14.2
5	55	30	15	2.89	19.0	3.03	15.1
6	50	35	15	2.89	20.4	3.04	16.2
7	55	25	20	2.87	18.3	3.02	14.0

8	50	30	20	2.92	18.3	3.07	14.1
9	45	35	20	2.91	19.8	3.06	15.8
$Al_2O_3 – ZrO_2$ additive							
1	65	25	10	2.91	19.9	3.04	16.3
2	60	30	10	2.99	19.7	3.12	16.3
3	55	35	10	3.03	20.5	3.17	16.8
4	60	25	15	2.96	18.5	3.11	14.4
5	55	30	15	3.03	18.7	3.17	14.9
6	50	35	15	3.05	20.0	3.20	15.9
7	55	25	20	2.96	18.5	3.13	14.0
8	50	30	20	3.04	18.3	3.20	13.9
9	45	35	20	3.07	19.4	3.25	14.8

Source: Authors

Density and porosity of the samples with $CaO – Al_2O_3 – Y_2O_3$, $MgO – Al_2O_3 – Y_2O_3$, and $Al_2O_3 – ZrO_2$ eutectic additives were quite close regardless of the additive content. As for mechanical characteristics, in otherwise equal conditions ceramics with $MgO – Al_2O_3 – Y_2O_3$ additive exhibited higher values than that with $CaO – Al_2O_3 – Y_2O_3$ or $Al_2O_3 – ZrO_2$ eutectics. This observation remained true for all investigated trimodal fraction ratios, which clearly favored magnesia-based additive. According to experimental data, increasing the content of $CaO – Al_2O_3 – Y_2O_3$, $MgO – Al_2O_3 – Y_2O_3$, and $Al_2O_3 – ZrO_2$ additives from 25 to 30% vol. had little effect on structural properties but significantly augmented bending strength of the material. Values obtained for the composition with 20% vol. n-SiC apprised LPSSiC armor parameters—almost zero open porosity and bending strength of 450 ± 25 MPa. Thus, the most efficient experimental batch for armor applications among those studied was the one containing 30% vol. of $MgO – Al_2O_3 – Y_2O_3$ eutectic additive and 20% vol. n-SiC dopant.

Table 5: Structural and mechanical properties of experimental samples containing n-SiC

Batch composition	**Parameters**		
	ρ, g/cm^3	**P_o, %**	**σ_{bend}, MPa**
15 % vol. n-SiC			
SiC + 25 % vol. $CaO – Al_2O_3 – Y_2O_3$	3.08	9.5	220 ± 25
SiC + 30 % vol. $CaO – Al_2O_3 – Y_2O_3$	3.12	8.0	200 ± 20
SiC + 25 % vol. $MgO – Al_2O_3 – Y_2O_3$	3.17	7.5	350 ± 15
SiC + 30 % vol. $MgO – Al_2O_3 – Y_2O_3$	3.29	5.0	310 ± 20
SiC + 25 % vol. $Al_2O_3 – ZrO_2$	3.22	8.5	285 ± 20
SiC + 30 % vol. $Al_2O_3 – ZrO_2$	3.36	6.5	300 ± 15
20 % vol. n-SiC			
SiC + 25 % vol. $CaO – Al_2O_3 – Y_2O_3$	3.33	1.2	380 ± 20
SiC + 30 % vol. $CaO – Al_2O_3 – Y_2O_3$	3.35	1.3	355 ± 15
SiC + 25 % vol. $MgO – Al_2O_3 – Y_2O_3$	3.42	0.4	450 ± 25
SiC + 30 % vol. $MgO – Al_2O_3 – Y_2O_3$	3.47	0.3	400 ± 25
SiC + 25 % vol. $Al_2O_3 – ZrO_2$	3.50	0.5	400 ± 20

SiC + 30 % vol. $Al_2O_3 – ZrO_2$	3.56	0.7	380 ± 20

Source: Authors

The experimental procedure also included studies of physico-mechanical features relevant to armor construction, i.e. fracture viscosity, elasticity modulus, and micro-hardness. The results are presented in Table 6. As expected, ceramics with n-SiC + 30% vol. $MgO – Al_2O_3 – Y_2O_3$ eutectic additive demostrated the highest performance capabilities and was adopted for armor material. Microstructure of such ceramics is shown in Figure 1.

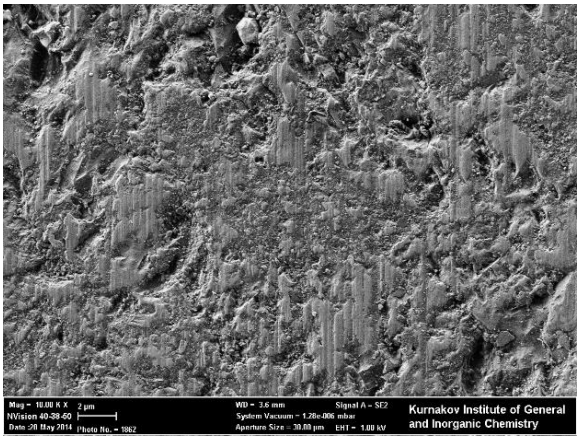
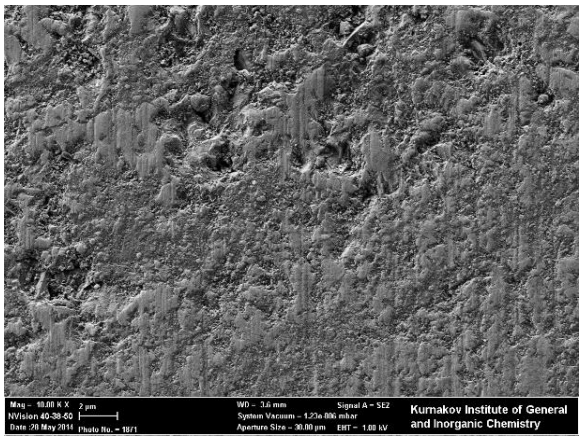
Table 6: Structural and mechanical properties of armor material containing 20% vol. n-SiC

Batch composition	Parameters		
	Fracture viscosity K_{1C}, MPa·m$^{1/2}$	**Elasticity modulus, GPa**	**Vickers hardness H_V, GPa**
SiC + 25 % vol. $CaO – Al_2O_3 – Y_2O_3$	3.8	345	18.4
SiC + 30 % vol. $CaO – Al_2O_3 – Y_2O_3$	3.7	340	18.6
SiC + 25 % vol. $MgO – Al_2O_3 – Y_2O_3$	4.0	380	19.4
SiC + 30 % vol. $MgO – Al_2O_3 – Y_2O_3$	4.2	360	18.8
SiC + 25 % vol. $Al_2O_3 – ZrO_2$	3.7	350	17.4
SiC + 30 % vol. $Al_2O_3 – ZrO_2$	3.6	340	17.0

Source: Authors

According to SEM data of specified ceramics, mean crystal size of silicon carbide was 3 – 6 μm; that of eutectic phases (alumomagnesian spinel, yttrium-aluminum garnet and corundum) was below 1 μm; nanoparticles of SiC did not exceed 60 nm. Closed porosity was mostly intercrystalline, about 1 – 2 % vol., with spherical pores; mean pore size was far below 1 μm.

Figure 1: Microstructure of armor ceramics samples (polished specimen, ×10000)

25 % vol. $MgO – Al_2O_3 – Y_2O_3$	25 % vol. $Al_2O_3 – ZrO_2$
	

Source: Authors

Another promising candidate for armor material would be ceramics with 30% vol. of $Al_2O_3 – ZrO_2$, (see Figure 1). According to SEM data of specified ceramics, mean crystal size of silicon carbide was 3 – 6 μm; that of eutectic phases was below 1 μm; sealed porosity was not observed. Particles of n-SiC did not exceed 60 nm.

Conclusion

In the present study, patterns of physico-mechanical and structural properties of silicon carbide ceramics were examined. SiC-based compositions with 20% vol. SiC nanopowder dopant and 30% vol. eutectic additives in $MgO – Al_2O_3 – Y_2O_3$ and $Al_2O_3 – ZrO_2$ systems were suggested for potential use in producing ceramics for armor applications. Specified ceramic materials had sintering temperature of 1900ºC; a fine-grain structure and depending of the eutectic additive exhibited bending strength of 450 ± 25 and 400 ± 20 MPa, microhardness of 18,8 and 17,0 GPa for magnesia-based and alumina-zirconia systems, respectively.

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