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# IMPROVEMENT OF MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HIGH DENSE SiC CERAMICS MANUFACTURED BY HIGH-SPEED HOT PRESSING

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Non-oxide ceramics possess high physical-mechanical properties, corrosion and radiation resistance, which can be used as a protective materials for radioactive wastes disposal. The aim of the present study was the manufacturing of high density SiC ceramics with advanced physical and mechanical parameters. The high performance on the properties of produced ceramics was determined by the dense and monolithic structure. The densified silicon carbide samples possessed good mechanical strength, with a high Vickers micro hardness up to 28.5 GPa.

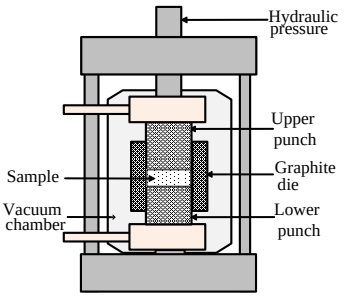
## INTRODUCTION

The problem of management of radioactive wastes (RAW) is of great importance. In this regard, the researches are carried out to develop radiation-resistant, high-strength ceramic and glass-ceramic materials for immobilization of RAW. To solve this actual problem, numerous studies on the development of non-oxide ceramics based on carbides, borides and nitrides by using of different producing methods were realized in KIPT. Non-oxide ceramics, in particular carbides, have high physical-mechanical properties, corrosion and radiation resistance, which make them perspective candidates for use as a barrier material in the system of RAW disposal. Several studies on the use of high-speed sintering methods as a manufacturing technique for SiC materials have been published in the last decade [1–7]. A new method of consolidation of powders for manufacturing of functional nanostructural, composite and gradient materials, is a Field Assisted Sintering Technology (FAST). Some variants of FAST method realization are high-speed hot pressing and high-speed sintering. The modified method of hot pressing with the electric fields assistance for fast heating and short duration of working cycle is the basement of high-speed consolidation process. In comparison with traditional technologies such as hot pressing (HP) and hot isostatic pressing (HIP), the method has some principal advantages for producing ceramic products with unique and tailored properties.

The most attractive features of the high-speed consolidation process are the enhanced densification and formation of highly dense, fine-grained, and homogeneous ceramics microstructure. The method advantage is also the possibility of solid-phase sintering process for high densification of ceramics without additional adhesion agents. The aim of the present study was the analyses of the influence of sintering temperature and holding time on densification, microstructure and mechanical properties of SiC ceramics manufactured by high-speed HP method.

## 1. MATERIALS AND METHODS

Pilot equipment for high-speed HP method realization was designed and put into operation in KIPT. The installation allows to realize a technological process for the sintering of powder materials of different compositions with high heating rate (350 °C/min) in both inert gas and vacuum (Fig. 1,a,b).




*a*

*b*

*Fig. 1. Scheme (a) and equipment for high-speed HP method (b)*

Nano sized powder of silicon carbide of 440 NDP brand with the average particle size ~ 440 nm (Superior Graphite Co, USA) was used as raw material. The powder particles with organic adhesion agent were formed as separated agglomerates of spherical form. The average agglomerates size was about 50 μm (Fig. 2).

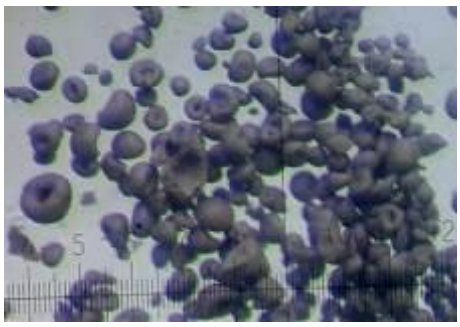


*Fig. 2. Nano sized powder of silicon carbide of 440 NDP brand*

For samples manufacturing, the initial powder was loaded into graphite die and sintered by high-speed HP method. The following process parameters were realized: heating rate was about 300…350 °C/min, sintering temperature was in the range 1950…2050 °C, pressure was 40 MPa. Experiments were carried out at different holding time and temperature regimes.

The following samples were investigated (Fig. 3):

– SiC (a, b) – sintering temperature at 1950 and 2050 ºC, holding time 10 min, pressure 40 MPa;

– SiC (c–f) – sintering temperature at 2050 ºC holding time 15, 20, 30, and 45 min, pressure 40 MPa.

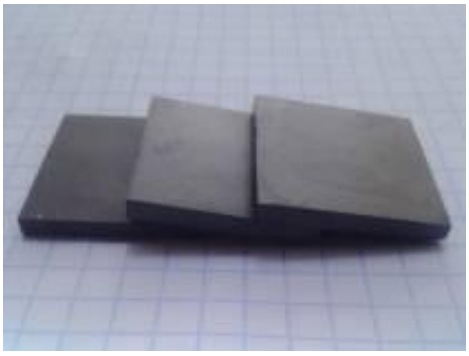


*Fig. 3. Samples of SiC ceramic (25x25 mm)*

The temperature was monitored by a radiation pyrometer focused at an upper punch of the die.

The bulk density of the blanks was measured using Archimedes principle.

Closed porosity was observed by means of XRD Tomography (Phoenix microme|x DXR-HD, GE Sensing & Inspection Technologies GmbH, Germany).

SiC samples were analyzed by scanning electron microscopy (SEM), (Zeiss EVO 40, Germany).

XRD spectra were obtained by diffractometer. The detection was made at a reflection focusing Bragg-Brentano.

To determine the breaking-load and the compressive strength of investigated samples tests were performed by means of breaking machine R-10 [8].

The microhardness of the SiC ceramics was determined by microhardness tester FM-800 (Future-tech Corp., UK).

## 2. RESULTS AND DISCUSSION

The sintering conditions and final properties of SiC samples manufactured by high-speed HP are presented in Tabl. 1. The relative densities of samples increased with sintering temperature. The possibility of the formation of liquid phase during sintering can assist in densification to achieve near full density with minimum grain growth [9–11]. The relative density of SiC ceramics was increased gradually from 98.7 to 99.4% during the holding time changing (10…30 min). The increase of holding time from 10 to 30 min at temperature 2050 ºC (sample SiC (e)) results in significant enhancing of material density parameters: apparent density, determined by hydrostatic weighing method, was about 3.19 g/cm$^3$ (99.4 % from theoretical value), closed porosity (0,6 %). In comparison, the apparent density of a SiC samples increased slightly from 3.16 to 3.17 g/cm$^3$, relative density from 98.4 to 98.7% and closed porosity (1.6…1.3%) with increase in temperature from 1950 to 2050 ºC and the same holding time 10 min.

Table 1

Physical properties of SiC ceramics

| Sample | Density ρ, g/cm$^3$ | Relative density ρ, % | Closed Porosity (calculated values), % |
|---|---|---|---|
| SiC – a | 3.16 | 98.4 | 1.6 |
| SiC – b | 3.17 | 98.7 | 1.3 |
| SiC – c | 3.18 | 99.0 | 0.9 |
| SiC – d | 3.18 | 99.1 | 0.9 |
| SiC – e | 3.19 | 99.4 | 0.6 |
| SiC – f | 3.19 | 99.4 | 0.6 |

Further holding time increasing up to 45 min has not significant effect on the physical properties, thus the sintering temperature 2050 ºC and holding time 30 min was selected as optimal technological regime for the manufacturing of SiC ceramics by high-speed hot pressing method.

XRD Tomography images of SiC ceramics are presented in Fig. 4 for SiC (a, b) produced at the different sintering temperatures (1950 and 2050 ºC) and the same holding time 10 min. The tomography results demonstrate that the closed porosity of ceramics was not significantly changed: from 1.6% SiC (a) to 1.3% SiC (b).

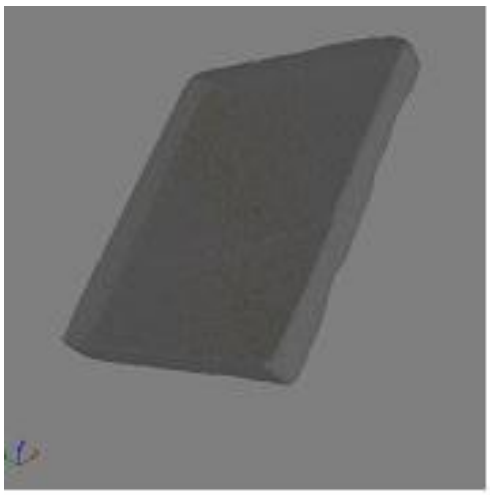


*Fig. 4. XRD Tomography of SiC – a*

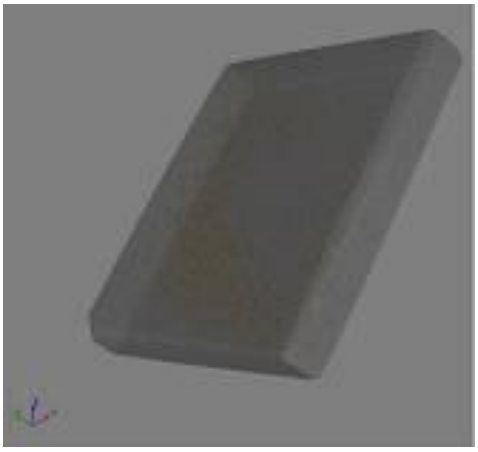


*Fig. 4. XRD Tomography of SiC – b*

On the contrary, images presented at Fig. 5 for SiC (c–e) demonstrate that closed porosity was principally decreased with holding time changing in the range 10…30 min at temperature 2050 ºC. Closed porosity of SiC (e) and SiC (f) samples was not observed by XRD Tomography method.

Prolonged holding time is force for pore rearrangement, coalescence, and removal. This process probably resulted in increased grain growth and partial densification. Compared to sample with holding time 10 min at temperature 2050 ºC (sample SiC (b)), pores were gradually removed by the prolonged holding time to 30 min (sample SiC (e)).

*Fig. 5. XRD Tomography of SiC – c*

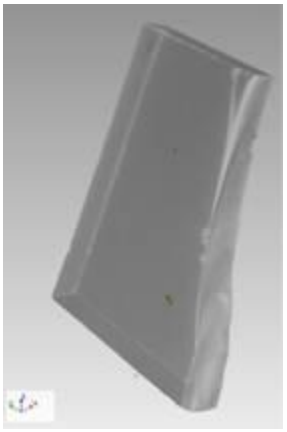


*Fig. 5. XRD Tomography of SiC – d*

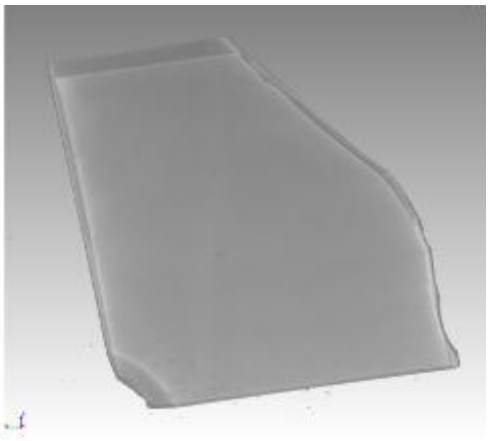


*Fig. 5. XRD Tomography of SiC – e*

Fractured surface micrographs of the sintered SiC ceramics are displayed in Fig. 6 for SiC (a, b). The microstructure analysis has demonstrated that increasing the temperature from 1950 to 2050 ºC with holding time 10 min is not sufficient for fine grain structure formation with clearly defined boundaries resulting in low density parameters. Apart from the grain size, the specimens processed at the same pressure and sintering temperature but other holding time exhibited different grain morphologies.

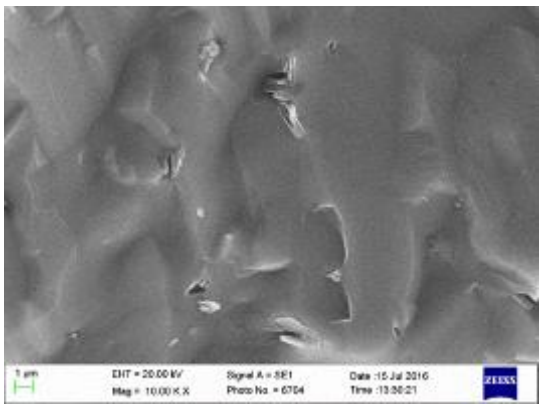


*Fig. 6. SEM of SiC – a*

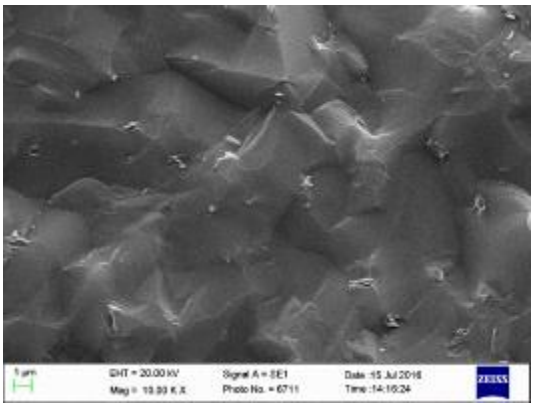


*Fig. 6. SEM of SiC – b*

In comparison, presented at Fig. 7 microstructures of the SiC (c–e) samples after holding time changing from 10 min to 30 min have demonstrated the formation of dense (90…99.4% of the theoretical density),

monolithic and uniform structure with clearly defined grain boundaries. The structures show features of the fragile destruction nature which probably resulted in further improvement of physical and mechanical properties of obtained SiC ceramics.

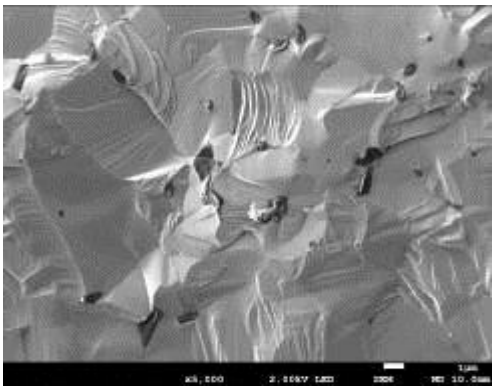


*Fig. 7. SEM of SiC – c*

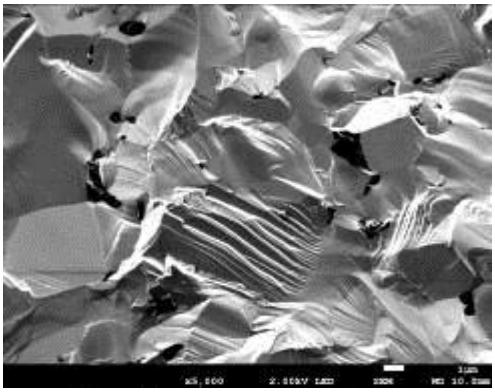


*Fig. 7. SEM of SiC – d*

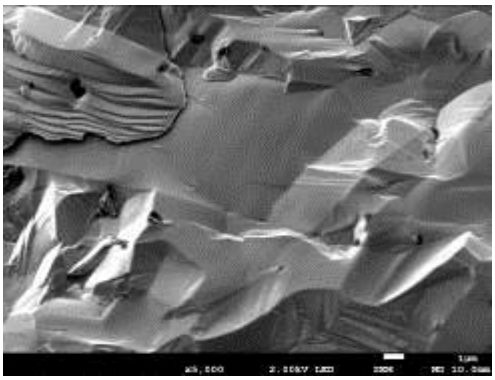


*Fig. 7. SEM of SiC – e*

SEM observations of the microstructure coincided well with the XRD Tomography and relative density results.

The high-speed sintering process results in a finer grained microstructure [12–13]. The theory applies to all rapid sintering techniques. This model is based on the assumption that densification and grain growth are thermally activated processes. The activation energy (ΔG) required for obtaining the atomic mobility necessary for sintering can be achieved by increasing temperature. The diffusion coefficient (D) increases significantly due to its direct relationship to temperature: $D \sim \exp(-\Delta G/kT)$, where k is the Boltzmann constant, T is the absolute temperature. The rapid heating to higher temperatures can be beneficial to achieve high density allied to fine grain size [14–16].

Phase identification of ceramics indicated that the manufactured ceramic materials were primarily the hexagonal 6H-SiC structures. XRD analysis of silicon carbide samples demonstrates the existence of two phases of SiC (hexagonal, polytypic modification) and carbon (graphite) content. XRD pattern of ceramic SiC (e) is shown at Fig. 8. The weak carbone traces were observed. The presence of carbon content on the XRD diffractogrames has not principal effect on the material properties.

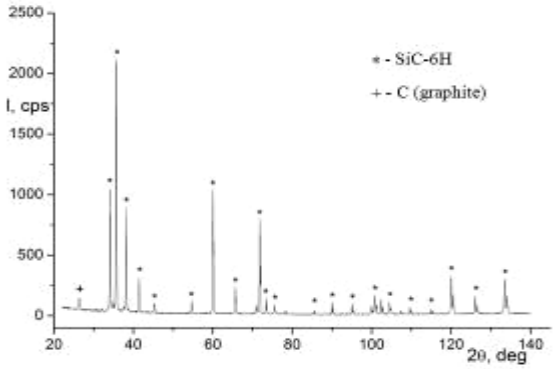



*Fig. 8. XRD of SiC – e*

The effect of sintering parameters on densification and mechanical properties has been studied in references [17–20]. The applied pressure and the sintering temperature have been identified as the main factors controlling the densification and influencing the mechanical properties of hot-pressed composites. The results of mechanical parameters presented in Tabl. 2 demonstrate that SiC ceramics manufactured at temperature 1950 ºC with holding time 10 min and at temperature 2050 ºC with holding time 10, 15, 20 min, showed no distinct differences and possessed relatively low values: compressive strength 1850…1950 MPa, Vickers micro hardness 22.9…26.5 GPa. The micro hardness of the SiC ceramic sintered at 2050 ºC with holding time 30 min (sample SiC (e)) was measured to be 28.5 GPa, which again confirmed that the sample is of high relative density.

Table 2

Mechanical properties of SiC ceramics

| Sample | Compressive strength σ, MPa | Micro hardness, GPa |
|---|---|---|
| SiC – a | 1850 | 22.9 |
| SiC – b | 1880 | 23.8 |
| SiC – c | 1930 | 25.9 |
| SiC – d | 1950 | 26.5 |
| SiC – e | 2000 | 28.5 |
| SiC – f | 2050 | 28.2 |

Further increasing of holding time up to 45 min did not lead to the principal improvement of mechanical properties of SiC ceramics. Results presented in Tabl. 2 demonstrate the possibility of manufacturing of SiC

ceramics with high physical-mechanical parameters by rapid hot pressing method.

## CONCLUSIONS

Optimal parameters for producing of high density ceramics based on SiC by high-speed hot pressing method have been determined.

The obtained ceramics present advanced physical-mechanical properties, such as, relative density $\rho = 98…99.5\%$ of the theoretical value, the porosity – 1.6…0.6%, the hardness – 265…2855 HV, the compressive strength $\sigma = 1850…2050$ MPa. The densified SiC samples manufactured at temperature 2050 ºC with holding time 30 min possessed the advanced parameters, such as, a good mechanical strength 2 $10^3$ MPa and a high Vickers micro hardness of 28.5 GPa.

SEM analysis was revealed that the high performance on the properties of SiC ceramics is determined by the dense and monolithic structure. X-ray studies have shown the presence of the 6H-SiC hexagonal structure in SiC ceramics.

Developed on the basis of silicon carbide high density ceramics are promising materials for use as a protective material in radioactive waste isolation, and other scientific and technical areas.

**Acknowledgements**

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## УСОВЕРШЕНСТВОВАНИЕ МИКРОСТРУКТУРЫ И МЕХАНИЧЕСКИХ СВОЙСТВ ВЫСОКОПЛОТНОЙ КЕРАМИКИ SiC, ПОЛУЧЕННОЙ МЕТОДОМ ВЫСОКОСКОРОСТНОГО ГОРЯЧЕГО ПРЕССОВАНИЯ

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Бескислородные керамические материалы демонстрируют высокие физико-механические свойства, коррозионную и радиационную стойкость, делающие их перспективными кандидатами для использования в качестве барьерных материалов для захоронения радиоактивных отходов. Целью настоящей работы было получение высокоплотной SiC-керамики с усовершенствованными физическими и механическими свойствами. Высокие параметры полученной керамики определяются формированием высокоплотной и монолитной структуры. Керамика карбида кремния обладает улучшенной механической прочностью и высокой твердостью по Виккерсу порядка 28,5 ГПа.

## ВДОСКОНАЛЕННЯ МІКРОСТРУКТУРИ ТА МЕХАНІЧНИХ ВЛАСТИВОСТЕЙ ВИСОКОЩІЛЬНОЇ КЕРАМІКИ SiC, ОТРИМАНОЇ МЕТОДОМ ВИСОКОШВИДКІСНОГО ГАРЯЧОГО ПРЕСУВАННЯ

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Безкисневі керамічні матеріали демонструють високі фізико-механічні властивості, корозійну та радіаційну стійкість, що роблять їх перспективними кандидатами для використання в якості бар'єрних матеріалів для захоронення радіоактивних відходів. Метою цієї роботи було отримання високощільної SiC-кераміки з вдосконаленими фізичними і механічними властивостями. Високі параметри отриманої кераміки визначаються формуванням високощільної і монолітної структури. Кераміка карбіду кремнію має поліпшену механічну міцність і високу твердість по Віккерсу порядка 28,5 ГПа