SiC- and Ti_3SiC_2-Based Ceramics Synthesis by Spark Plasma Sintering of Preceramic Paper

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Abstract. This paper is devoted to proposing a new approach to the synthesis of SiC- and Ti_3SiC_2-based ceramics by using of preceramic paper as a feedstock. A preceramic paper with SiC and Ti_3SiC_2 powder fillers were sintered by spark plasma sintering (SPS) method for holding time 10 minutes under pressure 20-100 MPa. The temperature for the sintering of SiC- and Ti_3SiC_2-filled paper was 2073-2373 K and 1373-1473 K respectively. The influence of sintering parameters on the materials microstructure was analyzed by scanning electron microscopy. It was revealed that with an increase in pressure from 20 to 100 MPa, the microstructure of the materials becomes denser. It agrees with the results of measuring the density of the sintering materials by the hydrostatic weighting. The determination of Young`s modulus by the acoustic method demonstrates that with the increase of the applied pressure during SPS, Young's modulus of the synthesized SiC- and Ti_3SiC_2-ceramics increase.

1. Introduction

Ensuring the safe operation of nuclear power plants is a key development factor for the nuclear industry. Largely, the safety of the facility during operation depends on the behaviour of the material from which it was made. The installations and constructions at nuclear facilities operate at high temperatures in the field of neutrons, γ-radiation, and fission fragments. The development of modern materials with properties corresponding to the nuclear industry requirements, is an urgent task, the solution of which will lead to the further development of the industry.

A number of studies are devoted to materials based on silicon carbide, considering their properties with the aim of further application of these materials in various industries. SiC has a number of unique properties providing stable operation of the equipment in aggressive environments, high temperatures, mechanical stress and radiation [1]. The use of this material in the nuclear industry will ensure the safe operation of nuclear facilities.

However, ceramic based on silicon carbide is brittle and difficult to mechanical processing, that will create certain difficulties in the design. The use of the MAX-phase can solve the problem. MAX phases belong to a relatively new class of refractory materials. In general, they are described by the formula $M_{n+1}AX_n$, where M is a transition metal, A is an element of the IIIA-IVA subgroup of the periodic system, X is carbon or nitrogen. The structural features of the MAX-phases determine a unique combination of the properties of metal and ceramics, such as high melting point, heat resistance, resistance to thermal

shocks, high elastic modulus, resistance to oxidation and corrosion, thermal conductivity and mechanical workability [2].

This paper focuses on the opportunity to synthesize paper-derived ceramic composites based on SiC and Ti_3SiC_2 by spark plasma sintering in a vacuum environment. The preceramic paper was used as the feedstock. It is a composite material, which is a matrix of organic cellulose fibers and inorganic powder filler, which is SiC or Ti_3SiC_2 powder [3]. It is assumed that the use of preceramic papers in high-temperature sintering will make it possible to obtain ceramic materials of a given shape and geometry. The physicochemical properties of materials will be possible to regulate by changing the filler concentration or sintering parameters to values corresponding to the requirements for finished products.

2. Materials and Methods

2.1. Sample preparation and sintering procedure

Preceramic paper is a multilayer composite material, the manufacturing process of which is associated with the use of a paper machine (Figure 1) and includes the following steps [3, 4]:

- the preparation of the original emulsion suspension containing filler and cellulose fiber;
- coagulation of fiber and filler in suspension using polymer additives;
- the formation of a sheet of paper by dehydration of the feedstock.

The technology of preceramic paper production in detail and its characteristics have been studied in ref. [5]. The composition of preceramic paper sheets for this study shown in Table 1.

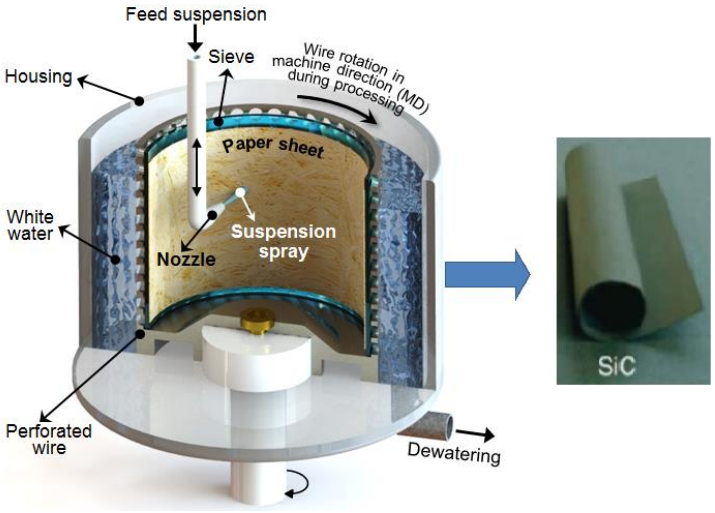

Figure 1. Schematic representation of a dynamic sheet former [4].

Table 1. Composition of the preceramic paper sheets with 90 wt% ceramic filler.

SiC- filled paper composition		Ti_3SiC_2-filled paper composition	
Cellulose fibers	13.14 %	Cellulose fibers	13.35 %
Powder SiC	144.00 %	Powder Ti_3SiC_2	164.70 %
Cationic Starch	1.61 %	Cationic Starch	1.80 %
Anionic Starch	0.16 %	Anionic Starch	1.80 %
Retention aid	1.09 %	Retention aid	1.40 %

Sintering samples were made in the form of 12 layers stack of the preceramic paper sheet, which was cut into rounds with a diameter of 20 mm. The sintering procedure was conducted using HPD25 SPS-equipment (FCT Systeme GmbH, Germany). The unique characteristic of this method is that powerful direct current pulses are passed through the sintering material. That creates a spark plasma discharge in

the gaps between the particles of the material. This contributes to the formation of interparticle contacts, which stimulates the diffusion process during the sintering of the material. The sintering of materials is conducted without the use of extra processing since the samples are subjected to pressure treatment before and during the sintering [6]. Sintering is conducted in a vacuum environment. The sintering modes of the samples are shown in Table 2.

Table 2. SPS-sintering parameters for samples of preceramic paper.

	SiC- filled paper	Ti_3SiC_2- filled paper
Pressure, MPa	20, 50, 100	20, 40, 50
Sintering temperature, K	2073, 2373	1373, 1473
Holding time, min	10	10

The samples sintered under these conditions, which are hard monolithic disks with a diameter of 19-22 mm, were subjected to mechanical surface treatment for further investigation. Mechanical surface treatment of the samples included grinding and polishing using silicon carbide papers (ISO from P1500 to P2000) on two sides of each sample. After polishing, the ceramic samples were treated in an ultrasonic bath with acetone for 15 minutes.

2.2. Hydrostatic weighing

For determination of sintered materials density, the hydrostatic weighting was used after treatment of the surfaces. The kerosene with a density 0.784 g/cm^3 (293 K) was used as a liquid during the hydrostatic weighting procedure.

2.3. Ultrasonic tomography

The ultrasonic tomography was supported by using an ultrasonic tomography system IdealSystem 3D. For scanning of the sintered samples, an ultrasonic single-channel sensor at 10 MHz was used. The results of tomography were processed by the Time of Flight (TOF) method. Database of ultrasonic tomography results was handled in the MATLAB package to determine Young`s modulus of sintered ceramics by the formula:

$$E = v^2 \cdot \rho, \quad (1)$$

where v – acoustic velocity of material;ρ – density of material.

2.4. Scanning electronic microscopy

The microstructure and elemental composition of the sintered materials surface were investigated by scanning electron microscopy (SEM) using Vega 3 (Tescan, Brno, Czech Republic) equipped with energy-dispersive X-ray spectroscopy attachment.

3. Results and Discussion

3.1. Hydrostatic weighing results

Table 3 includes the results of density determination for the sintered materials. The obtained results demonstrate the growth of materials density by increasing sintering pressure. This dependent is correct for both materials.

3.2. Young`s modulus

After ultrasonic tomography, the database of ultrasonic signals from the sensor was analysed by using MATLAB software package. The main informational characteristic of TOF method is an ultrasonic wave trip-time from sample surface to back side The acoustic velocity of sintered materials was determined from the sample thickness correlation with the trip-time. Then it becomes possible to

calculate the value of Young's modulus for each sample by Formula (1). The calculation results are presented in Table 4.

Table 3. Hydrostatic weighting results for the sintered samples.

SiC-based ceramic composite			
Pressure, MPa	Water absorption, %	Porosity, %	Density of sample, g/sm^3
20	14.61	62.8	2.059
50	11.20	30.9	2.228
100	3.36	13.4	2.749
Ti_3SiC_2-based ceramic composite			
Pressure, MPa	Water absorption, %	Porosity, %	Density of sample, g/sm^3
20	5.90	35.7	3.140
40	3.93	22.0	3.579
50	2.07	11.1	4.039

Table 4. Results of TOF and determination of acoustic signal trip-time and Young`s modulus of the samples.

SiC-ceramics			Ti_3SiC_2-ceramics		
Pressure, MPa	Acoustic velocity, m/s	Young`s modulus, GPa	Pressure, MPa	Acoustic velocity, m/s	Young`s modulus, GPa
20	7823	126	20	5250	90
50	10004	223	40	6270	140
100	10306	292	50	6950	195

Based on the analysis results, it follows that the increasing of the sintering pressure contributes to an increasing of the acoustic velocity and Young's modulus of the synthesized material. It can be explained by samples density increasing. The obtained values of the acoustic velocity in the synthesized materials are lower than for monolithic SiC- and Ti_3SiC_2-ceramics [7], which is attributed to the higher porosity of the sintered materials.

3.3. Scanning electronic microscopy

An analysis of the change in the microstructure (Figures 2) of the SiC samples showed that with an increase in sintering temperature from 2073 to 2373 K and pressure in the range from 20 to 100 MPa, the microstructure of the material becomes denser, which also agrees well with the results of measuring the density of the samples. It should be noted that a temperature of 2073 K is insufficient for the synthesis of SiC ceramics since the powder particles are practically not connected to each other. In addition, elongated pores formed by the decomposition of cellulose fibers can be observed at low pressure.

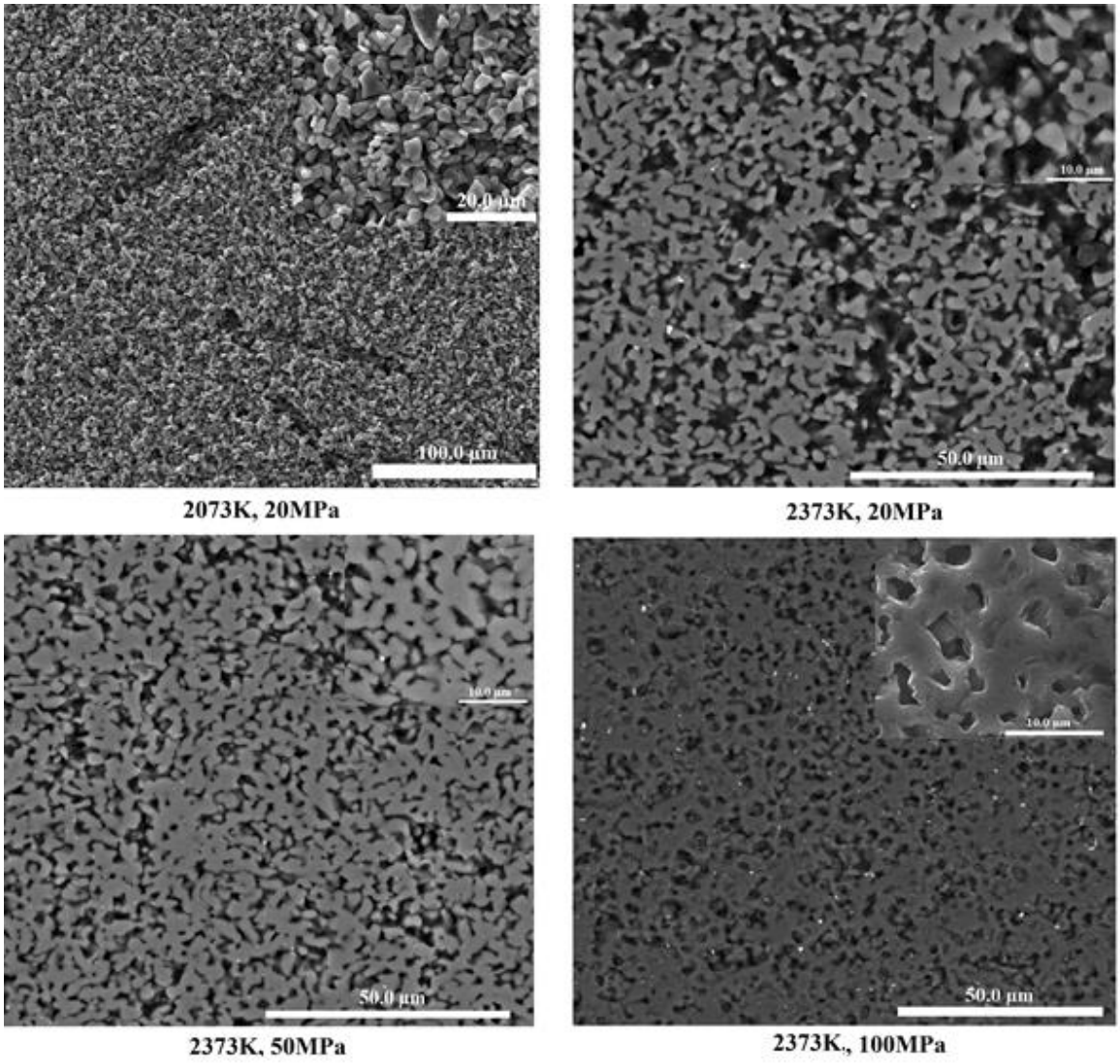

Figure 2. Surface SEM images of the sintered SiC-based ceramic materials.

When studying the microstructure of the MAX-phase sample (Figure 3) sintered at a temperature of 1373 K and pressure of 20 MPa, a high porosity of the surface of the sample was detected. It can be explained by the fact that the powder particles did not sintered completely at this value of temperature. However, the elongation pores from decomposed cellulose were not observed on the surface of the sample, in contrast with SiC ceramics.

The increasing of sintering temperature to 1437 K makes the process of powder particles sintering more intense. It results in a decrease in the surface porosity of the materials. While maintaining the sintering temperature of 1473 K, the MAX-phase density increases depending on the sintering pressure of the preceramic paper.

The results of microstructure analysis completely coincide with the results presented in 3.1.

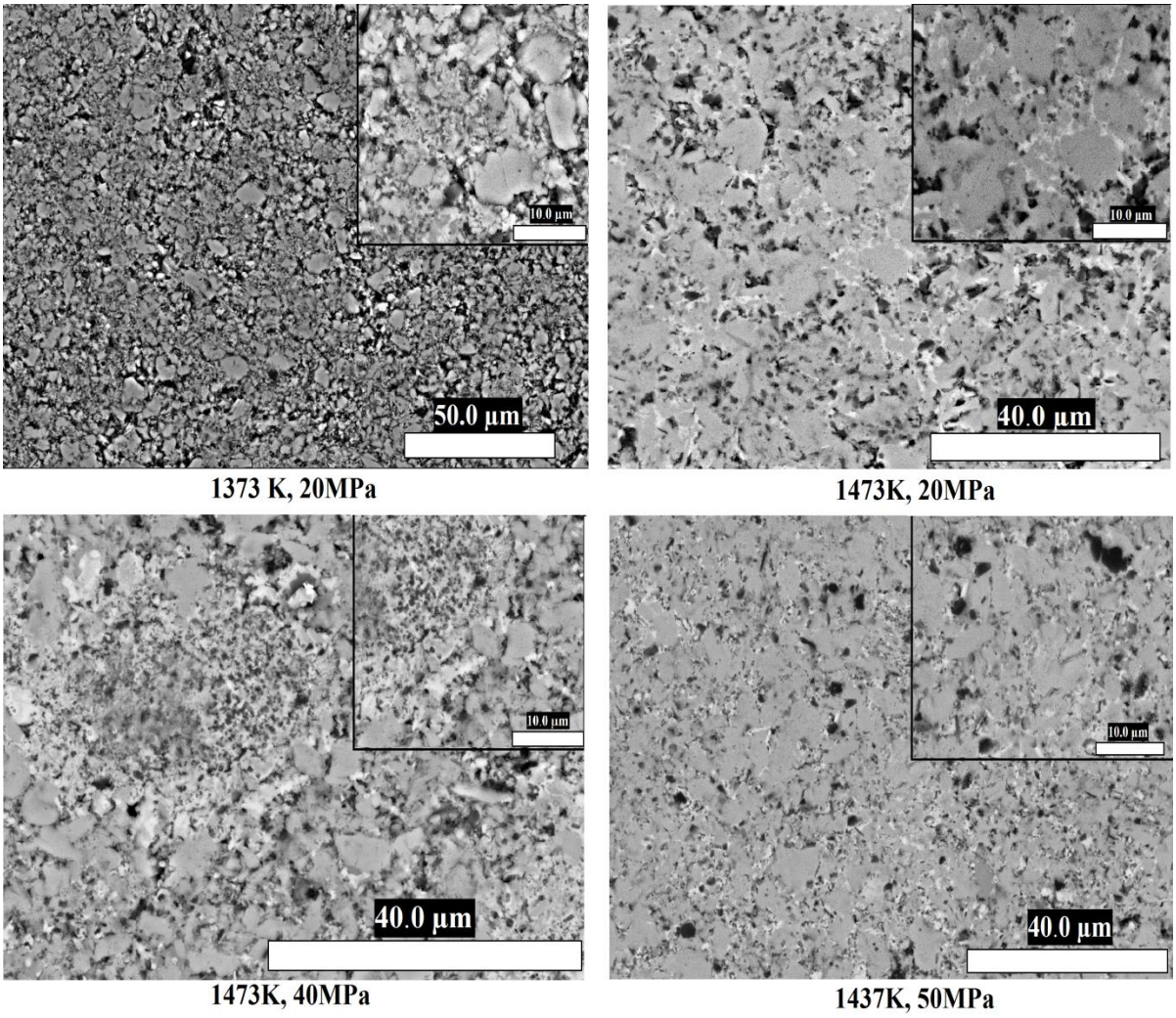

Figure 3. Surface SEM images of the sintered Ti_3SiC_2-based materials.

Conclusion

The ceramic materials were synthesized by SPS of preceramic papers with SiC and Ti_3SiC_2 powder filler at 2073-2373 K and 1373-1473K, respectively, under 20-100 MPa pressure for 10 minutes successfully.

An increase in the sintering pressure of preceramic papers from 20 to 100 MPa leads to densification of the microstructure and a decrease in the open porosity of the samples, which leads to an increase in the mechanical characteristics of the material.

Spark plasma sintering provides to the decomposition of cellulose fibers, pores of which are not observed at a sintering temperature of 1473 K and high pressures in case of Ti_3SiC_2-based ceramics and at 2373 K for SiC-ceramics.

Further researching will be focused on the synthesis of non-porous SiC and Ti_3SiC_2-based ceramic composites, as well as the creation of tubular composite materials based on SiC reinforced with silicon carbide fibers.

Acknowledgments

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