

# Influence of preceramic paper composition on microstructure and mechanical properties of spark plasma sintered $\text{Ti}_3\text{SiC}_2$ -based composites

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**Abstract.** This paper describes the effect of preceramic paper composition on microstructure and mechanical properties of  $\text{Ti}_3\text{SiC}_2$ -based composites. The preceramic paper with  $\text{Ti}_3\text{SiC}_2$ -powder filler and different content (from 10 to 40 wt.%) of organic component (cellulose) was prepared. The composites were obtained by spark plasma sintering (SPS) at 50 MPa pressure for 10 min holding time. The sintering temperature was 1473 K. The influence of organic content on microstructure, phase composition, and flexural strength of the sintered materials was analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and mechanical testing, respectively. It was revealed that the microstructure of the sintered materials became more porous with increasing of cellulose content in the paper. XRD analysis showed the presence of  $\text{Ti}_3\text{SiC}_2$ , TiC and  $\text{TiSi}_2$  phases in the sintered samples while the content of the  $\text{Ti}_3\text{SiC}_2$  phase increase with decreasing of the organic content. The flexural strength changes from 100 (40 wt.%) to 300 MPa (10 wt.% organic binder) that is caused by porosity of the composites.

## 1. Introduction

MAX-phases belonging to the class of heat-resistant materials are generally described by the formula  $\text{M}_{n+1}\text{AX}_n$ , where M is the transition metal, A is the element of the IIIA-IVA subgroup of the periodic system, X is the carbon or nitrogen. The  $\text{Ti}_3\text{SiC}_2$ -based MAX-phase composite is a well-studied compound and is of great interest to the modern industry from a practical point of view. Structural features of this compound cause a unique combination of the metal and ceramics properties, such as high melting point, resistance to thermal shock, high elastic modulus, resistance to oxidation and corrosion, thermal conductivity and machinability [1, 2].

The possibility of fabrication of  $\text{Ti}_3\text{SiC}_2$ -based composites by spark plasma sintering (SPS) using preceramic papers with inorganic  $\text{Ti}_3\text{SiC}_2$  powder fillers as a feedstock has been shown in [3]. It is assumed that the application of preceramic papers in high-temperature sintering will provide the opportunity to obtain gradient ceramic materials with complex shape and geometry. The properties of such materials can be controlled by changing the paper composition or sintering parameters. Currently, there is no data on the preceramic paper composition effect on the synthesis of composites by SPS method. Thereby, influence of the organic binder content in preceramic papers on the microstructure, phase composition and flexural strength of the sintered composites was studied.

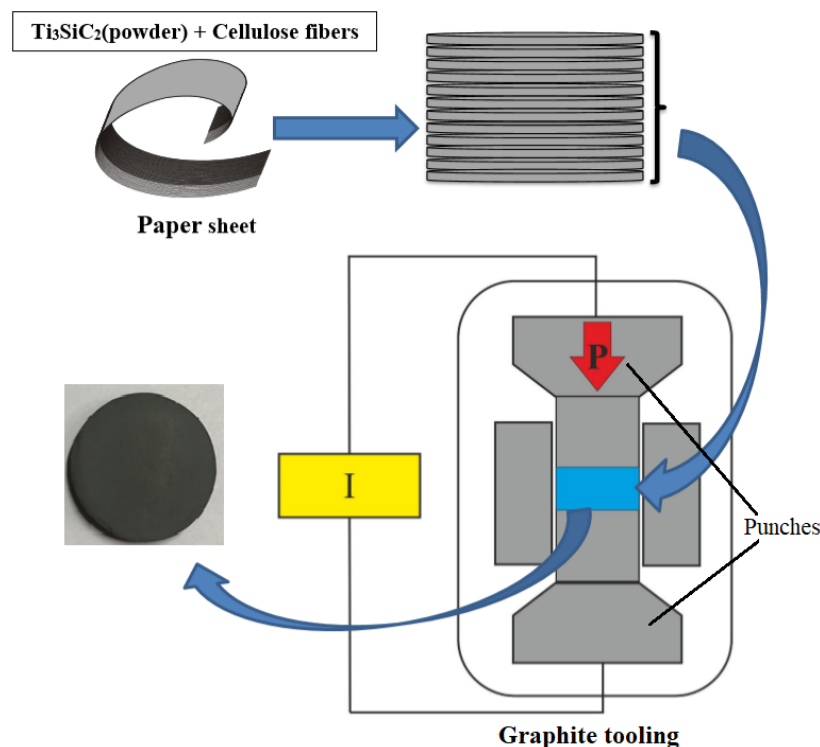


## 2. Materials and Methods

### 2.1. Sample preparation and sintering procedure

The preceramic paper sheets with  $\text{Ti}_3\text{SiC}_2$  powder filler were fabricated by a laboratory dynamic hand-sheet former (Dynamic hand-sheet former D7, Sumet Systems GmbH, Germany). The fabrication process is clearly described in paper [4].

The composite materials were fabricated by spark plasma sintering SPS 10-4 (Advanced Technology, USA). A preform consisting of several layers of preceramic paper was placed between two punches in graphite die as it is shown in Figure 1.



**Figure 1.** Schematic representation of fabrication process of  $\text{Ti}_3\text{SiC}_2$ -based materials from preceramic papers.

The sintering was performed in a vacuum under conditions summarized in Table 1. An extra processing was not performed since the samples was subjected to pressure treatment before and during the sintering [5]. The content of cellulose fibers in preceramic paper was varied from 10 to 40 wt.%.

**Table 1.** Cellulose content and SPS parameters.

Cellulose content [wt.%]	SPS-sintering parameters	
10	Pressure [MPa]	50
20	Sintering temperature [K]	1473
30	Holding time [min]	10
40		

Dense monolithic disks of the sintered  $\text{Ti}_3\text{SiC}_2$ -based materials with a diameter of 20 mm were subjected to mechanical surface treatment by grinding and polishing for further characterization. The grinding and polishing procedures were performed using silicon carbide papers (ISO from P80 to P2000) on both sides of each sample. Finally, the samples were cleaned in an ultrasonic bath with acetone for 15 min.

## 2.2. Characterization

The phase composition was analyzed by X-ray diffraction using Shimadzu XRD 7000S diffractometer ( $\text{CuK}\alpha$  radiation) equipped with OneSight high-speed 1280-channel detector. The surface microstructure of the materials was studied by scanning electron microscopy using EVO 50 XVP (Zeiss, Germany) microscope. The apparent density of the composites was measured by Archimedes' method. For the measurement, the kerosene with a density of  $0.784 \text{ g/cm}^3$  (293 K) was used.

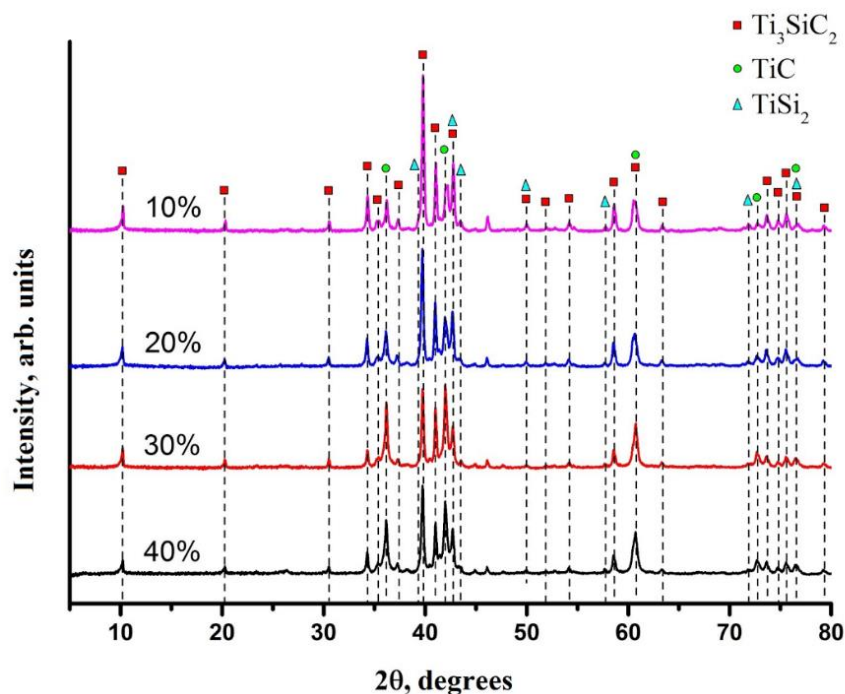
## 2.3. Mechanical testing

The flexural strength of the sintered  $\text{Ti}_3\text{SiC}_2$ -based composites was measured using a Gotech al7000m testing machine. The measurements were performed according to the Borger et.al. [6] method using a special device for small punch strength tests [7]. After XRD and SEM analysis, each sample was cut into a five samples with a diameter of 8 mm and a thickness of 1 mm. The sample was mounted on the support ring of the device so that its middle was located in the centre of the inner diameter of the ring, and its longitudinal axis was perpendicular to the direction of loading with the tip of the punch.

## 3. Results and Discussion

### 3.1. X-ray diffraction

The analysis of diffraction data revealed a strict regularity in the phase content changes depending on the organic binder content in the preceramic paper (Figure 2). It was found that a change in the content of cellulose in the range from 10 to 40 wt.% leads to a decrease in the content of the  $\text{Ti}_3\text{SiC}_2$  phase from 69.4 to 49 vol.% (Table 2), respectively. Along with the decrease of the MAX-phase content, an increase in the volume content of the TiC and  $\text{TiSi}_2$  phases is observed. Partial decomposition of the  $\text{Ti}_3\text{SiC}_2$  is due to an increase in the concentration of additional carbon formed as a result of fibers decomposition. Thus, it was found that the additional carbon can react with the  $\text{Ti}_3\text{SiC}_2$  phase leading to its partial decomposition and the formation of TiC and  $\text{TiSi}_2$  phases.



**Figure 2.** Diffraction patterns of  $\text{Ti}_3\text{SiC}_2$  composites obtained by SPS of preceramic paper with 10, 20, 30, 40 wt.% of organic binder at 50 MPa, 1473 K.

**Table 2.** Phase composition, lattice parameters and crystallite size of the samples.

Sample	Phase	Phase content [vol.%]
Ti <sub>3</sub> SiC <sub>2</sub> _10 wt.%	Ti <sub>3</sub> SiC <sub>2</sub>	69.4
	TiC	18.4
	TiSi <sub>2</sub>	12.2
Ti <sub>3</sub> SiC <sub>2</sub> _20 wt.%	Ti <sub>3</sub> SiC <sub>2</sub>	67.2
	TiC	28.0
	TiSi <sub>2</sub>	4.8
Ti <sub>3</sub> SiC <sub>2</sub> _30 wt.%	Ti <sub>3</sub> SiC <sub>2</sub>	52.8
	TiC	40.8
	TiSi <sub>2</sub>	6.4
Ti <sub>3</sub> SiC <sub>2</sub> _40 wt.%	Ti <sub>3</sub> SiC <sub>2</sub>	49.0
	TiC	48.4
	TiSi <sub>2</sub>	2.6

### 3.2. Hydrostatic weighing results

Table 3 shows the results of density and porosity measurements of the sintered materials. The obtained results demonstrate that the powder particles in the preceramic paper consolidate more strongly (lower porosity) as the powder filler content increases. This is also confirmed by the SEM data presented below. The density of composites increases from 2.65 to 4.04 g/cm<sup>3</sup> as the proportion of organic component decreases.

**Table 3.** Hydrostatic weighting results for the sintered samples

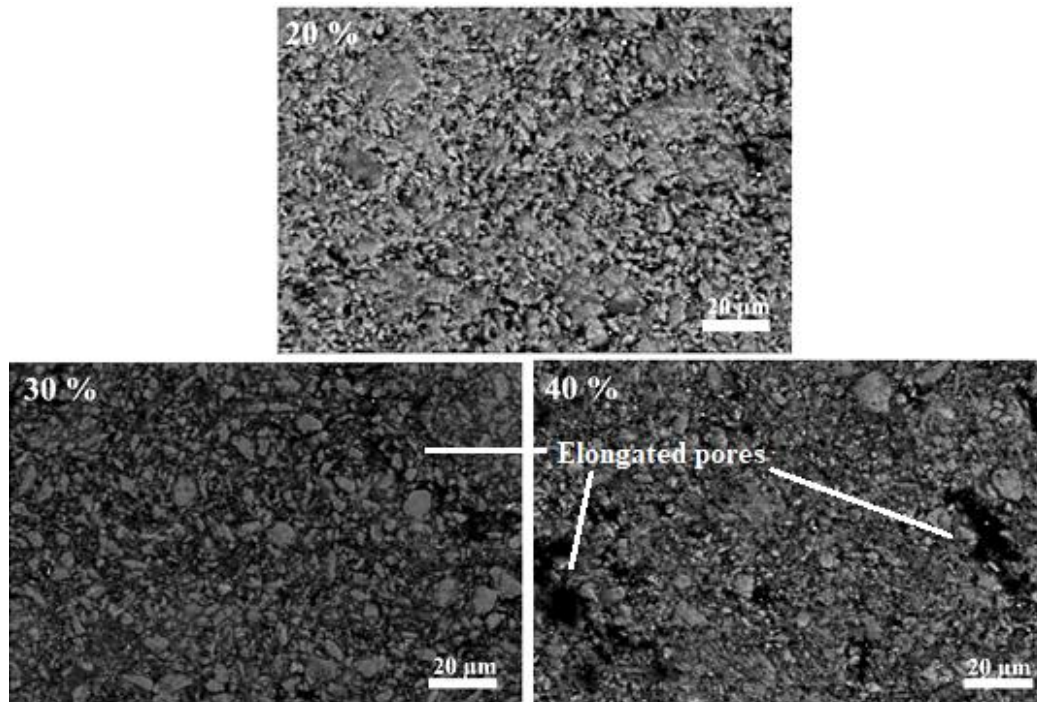
Cellulose content [wt.%]	Water absorption [%]	Porosity [%]	Density of sample [g/cm <sup>3</sup> ]
10	1.9	11.1	4.04
20	9.0	48.9	2.82
30	7.7	38.9	2.81
40	6.7	29.2	2.65

### 3.3. SEM analysis

The analysis of SEM images (Figure 3) shows a significant difference in the microstructure of the samples depending on the content of cellulose in the preceramic paper. Decrease in the fraction of cellulose in the sintered paper leads to compaction of the material and, consequently, to a decrease in its porosity (dark areas) at sintering temperature of 1473 K. Elongated pores can be seen in the structure of composites sintered from preceramic paper with 30 and 40 wt.% of cellulose. Such pores begin to collapse with increasing sintering pressure and are not observed in composites obtained from preceramic papers with 10 wt.% of cellulose at 50 MPa as shown in [3].

### 3.4. Flexural strength

The flexural strength of composites sintered at 1473 K (50 MPa) was increased from 100 to 120 MPa with decreasing cellulose content from 40 to 20 wt.%. Such low values are due to the high porosity of such composites (see Table 3). Decrease in the proportion of organic component to 10 wt.% leads to increase in the strength of composites (sintered at the same parameters) up to 300 MPa.



**Figure 3.** Surface SEM images of the sintered  $\text{Ti}_3\text{SiC}_2$ -based materials.

### Conclusion

The influence of preceramic paper composition on microstructure and phase composition of spark plasma sintered  $\text{Ti}_3\text{SiC}_2$ -based composites was studied. It was found that the increase in the content of organic component in the preceramic paper leads to phase redistribution in the sintered composites: decreasing MAX phase and increasing TiC content. Flexural strength of the composites sintered from preceramic paper with cellulose content of 20-40 wt.% was only 100-120 MPa, which is due to its low density (2.65-2.82 g/cm<sup>3</sup>). The decrease of cellulose content leads to fabrication of more dense (4.04 g/cm<sup>3</sup>) composites with significantly higher flexural strength (300 MPa). Varying the composition of preceramic papers provides the possibility to obtain composites with different microstructures, which can be used for manufacturing of composites with gradient porosity.

### Acknowledgments

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