# Formation of gradient porous composites from preceramic papers with $Ti_3SiC_2$ powder filler

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**Abstract**. This article is devoted to fabrication of gradient $Ti_3SiC_2$-based composites using preceramic papers as a feedstock. The initial raw material is a stack of preceramic paper with a $Ti_3SiC_2$ powder filler, the content of which varies from 60 to 90% every three layers. The composites were obtained by spark plasma sintering (SPS) method at 10 MPa pressure for 10 min holding time. The sintering temperature was 1250 °C. The microstructure and phase composition of the obtained gradient composites were analyzed.

## 1. Introduction

One of the recent topics in modern industry is the development of new composite materials with variable structure and properties. These materials include composites with MAX-phases, generally described as $M_{n+1}AX_n$, where $M$ – transition metal, $A$ – element of IIIA-IVA group, $X$ – carbon or nitrogen, $n$ – 1…4. MAX phases have high electrical and thermal conductivity, low friction coefficients, high strength combined with low density, high resistance to damage, oxidation and thermal shock [1-3]. In addition, these materials exhibit plastic properties at high temperatures and are easily machined.

One of the most promising methods for synthesis of composite materials is spark plasma sintering (SPS), which allows obtaining materials in a short period of time [4]. It is considered that the use of preceramic papers as a raw material allows the fabrication of materials and products with complex shapes, whose physical and mechanical properties can be tailored by changing the composition of the papers and sintering parameters [5].

In the previous work [6], the effect of the fraction of powder filler in preceramic paper on microstructure and mechanical properties of the resulting $Ti_3SiC_2$-based composites was studied. It was shown that different microstructure (porosity) can be formed by changing the composition of the preceramic paper. In the current work, we consider the possibility of fabrication composite materials with gradient porosity by the SPS method using preceramic papers with $Ti_3SiC_2$ powder filler.

The purpose of this work is to fabricate gradient composite materials from preceramic papers with a volume content of $Ti_3SiC_2$ powder filler of 60-90 wt% and to study their microstructure and mechanical properties.

## 2. Materials and Methods

### *2.1. Preparation of composites*

Preceramic paper sheets filled with $Ti_3SiC_2$ powder were manufactured using D7 hand sheet former machine (Sumet Systems GmbH, Denklingen, Germany) [5]. The concentration of the powder filler in the paper was increased from 60 to 90 wt.% every three layers. The schematic diagram of the preparation process is shown in Figure 1.

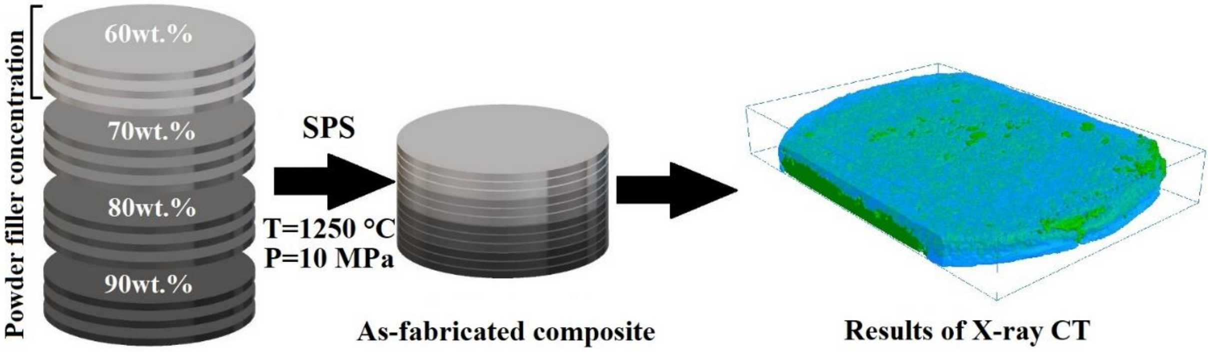


**Figure 1.** Scheme stacking layers preceramic paper before sintering process

The sintering of composite materials was carried out by spark plasma using SPS 10-4 machine (Advanced Technology, USA). The prepared stack of preceramic paper was placed between two punches in a graphite die. Graphite paper was placed between the die and the samples to ensure good current conductivity and to limit the chemical reaction of the die with the sintering material. Sintering was carried out in vacuum at the temperature of 1250 °C and pressure of 10 MPa. The sintered samples were monolithic disk with a diameter of 20 mm. The macrostructure of the samples was investigated by X-ray tomography (Fig.1), where the porous structure of the sample is highligted in blue, and the dense structure – in green.

*2.2. Characterization*

The phase composition of the samples was studied by X-ray diffraction using XRD 7000S (Shimadzu, Kyoto, Japan) diffractometer equipped with a high-speed 1280-channel OneSight detector (Shimadzu, Kyoto, Japan). The microstructure and elemental composition of the surfaces of the materials were analyzed by scanning electron microscopy (SEM) using EVO 50 XVP (Zeiss, Germany) equipped with energy-dispersive X-ray spectroscopy (EDS) attachment. The hardness of the sintered samples was measured at a load of 29.4 N by the Vickers method using microhardness tester (KB 30S Prüeftechnik, Germany). The fracture toughness of the samples was measured using indentation crack length (ICL) method [7].

## 3. Results and discussion

*3.1. Phase composition*

Figure 2 shows the results of X-ray diffraction analysis of the sintered composite from both sides of the sample ($Ti_3SiC_2$ – 60% and $Ti_3SiC_2$ – 90%). The diffraction pattern of the surface with the powder filler content of 60 wt.% consists of $Ti_3SiC_2$ and TiC phases, which volume content is 15 and 85%, respectively. It can be seen that the $Ti_3SiC_2$-90% side consists of $Ti_3SiC_2$, TiC and $TiSi_2$ phases with the volume ratio of 32 %, 49 % and 19 %, respectively. It is assumed that the absence of the $TiSi_2$ phase in the top layer of the sample is associated with its transition to the liquid phase at the sintering temperature of 1250°C. Through the diffusion process, $TiSi_2$ can precipitates in deeper layers of the sample [8,9].

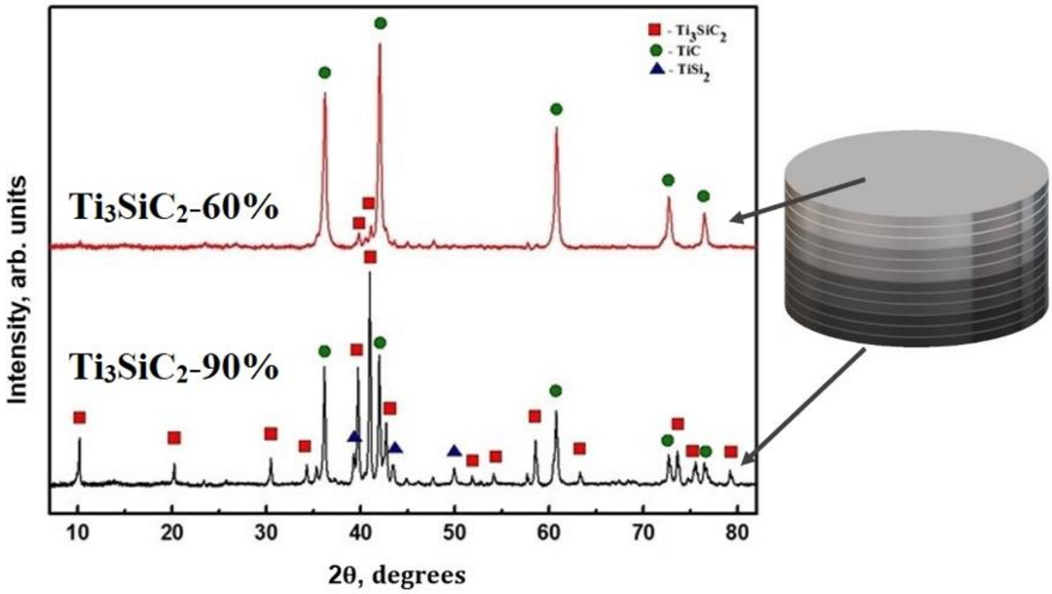


**Figure 2.** Diffraction patterns of the surfaces of the sample $Ti_3SiC_2$-60% and $Ti_3SiC_2$-90%

*3.2. Microstructure and mechanical properties*

Figure 3 shows the SEM images and EDS elemental maps of the cross-section of the sintered composite. A significant difference was found in the microstructure of the material depending on the concentration of the powder filler in the preceramic paper. Increasing the amount of powder filler in the feedstock leads to an increase in its density. Therefore, the gradient porous microstructure was formed in the composite. The strong decomposition of the $Ti_3SiC_2$ in the regions with low filler content explains the appearance of material inhomogeneity (upper layer in Figure 3).

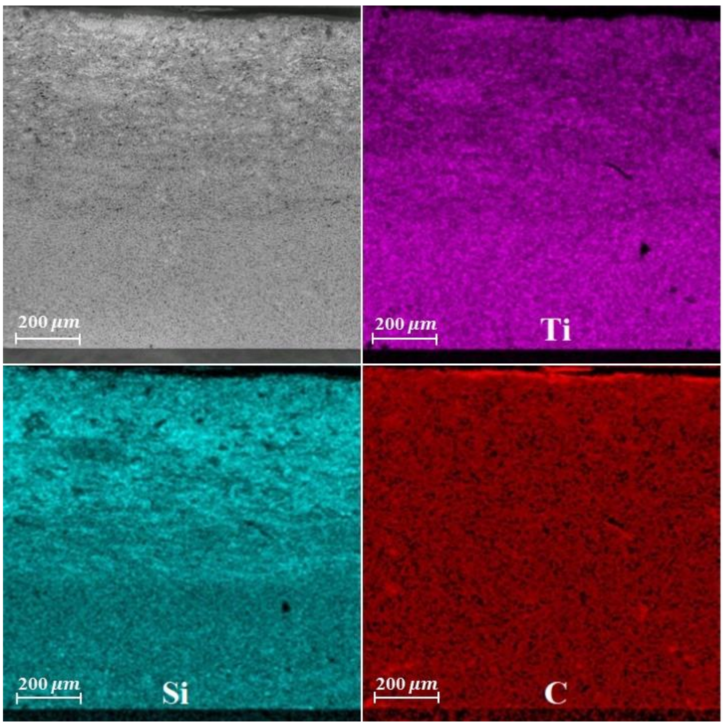


**Figure 3.** Cross section SEM images of the sintered composite

The EDS results show the presence of regions with a higher silicon content and a lower titanium content, which corresponds to the $TiSi_2$ phase. The phase with the high Ti content corresponds to the MAX phase [6].

The Vickers microhardness of the sample changes from 2.1 to 8.2 GPa at the move from the more porous to the denser side of the sample, i.e. with an increase in the amount of powder filler from 60 to 90 wt.%. It is also noteworthy that it was not possible to calculate the fracture toughness for the porous surface of the sample ($Ti_3SiC_2$-60%), while this value was 5.4 $MPa{\cdot}m^{1/2}$ for the side with denser microstructure.

## 4. Conclusion

Composites with porosity gradient were fabricated by forming a layered structure from preceramic paper with a variable fraction of powder filler. Within the framework of the study, the effect of the content of filler in preceramic paper on the microstructure, phase composition and hardness of the sintered composite was studied. It was found that an increase in the filler volume fraction in the preceramic paper from 60 to 90% leads to an increase in the MAX phase fraction and a decrease in the carbide phase fraction. Application of preceramic papers with variable composition can be promising way to obtain composites with gradient porosity and composition.

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## References

[1] Lyu J, Kashkarov E B, Travitzky N, Syrtanov M S and Lider A M 2021 *J. Mater. Sci.* **56** 1980–2015
[2] Barsoum M W 2000 *Prog. Solid. State Ch. chemistry* **28** 201–281
[3] Sun Z M 2011 *Int. Mater. Rev.* **56** 143–166
[4] Papynov E K 2016 *Bull. Far East. Branch Rus. Acad. Sci.* **6** 190
[5] Travitzky N 2008 *J. Am. Ceram. Soc.* **91** 3577-92
[6] Sedanova, E P, Kashkarov E B, Syrtanov M S, Abdullina K R, Mingazova Y R, Lider A M and Travitzky N 2020 *J. Phys.: Conf. Ser.* **1611** 012007
[7] Anstis G R, Chantikul P, Lawn B R, Marshall D B 1981 *J. Am. Ceram. Soc.* **64** 533–538
[8] Kashkarov E B, Syrtanov M S, Sedanova E P, Ivashutenko A S, Lider A M and Travitzky N 2020 *Adv. Eng. Mater* **22** 2000136
[9] Krotkevich D G, Kashkarov E B, Syrtanov M S, Murashkina T L, Lider A M, Schmiedeke S and Travitzky N 2021 *Ceram. Int.* **47** 12221-27