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RESEARCH ARTICLE

Role of sintering conditions on structural and mechanical properties of carbon fiber fabric reinforced ZrB_2-Sic composites

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Abstract: In this study, the effects of sintering conditions on the structural and mechanical properties of spark plasma sintered ZrB2-based composites were investigated in detail. In addition, to observe the impact of the binder, the binder was used in some materials. Thus, the effects of binder on the properties of composites while preparing ceramic slurry were tested. The effects of the sintering conditions of the materials prepared at different temperatures and stages on the composites were examined in detail. The densities, phase developments, microstructure analyses and mechanical properties of the composites were determined by the Archimedes principle, X-Ray Diffraction, Scanning Electron Microscopy, and three-point bending test, respectively. It was found that the samples sintered in double-stage and containing binder exhibited a denser microstructure. Similarly, it was observed that the mechanical properties were improved by using both double-stage sintering and binder.

Keywords: Ceramic matrix composites, Carbon fiber, Spark plasma sintering, Microstructure, Three-point bending test.

1. Introduction

Zirconium diboride (ZrB_2) is a preferred material for use on the sharp surfaces of hypersonic aircraft. Due to its high melting point, ZrB_2 is used in parts such as engine hood inlets, wing front edges, and nose cavities that must withstand temperatures of 1900-2500°C. SiC is a promising material in engineering applications requiring high temperatures due to its excellent mechanical properties at high temperatures, high thermal conductivity, high corrosion, and wear resistance. However, application fields of SiC remain limited due to its low fracture toughness. To overcome the low fracture toughness of SiC ceramics, fiber is added to the SiC matrix [1]. It has been proven that adding SiC to ZrB_2 increases its oxidation resistance and limits diboride grain growth [2].

Although the ZrB_2–SiC material has been developed, its use has many problems in large-scale applications. First, parts with complex shapes and high density are difficult to shape, fabricate and sinter due to their strong covalent bonds. Carbon is used as an additive to improve the thermal tensile strength of the ZrB_2-SiC system. However, the low fracture toughness and low thermal shock resistance properties still need to be improved. Therefore, the use of a fiber reinforcement phase can be exploited to increase the fracture toughness of the ZrB_2-SiC material, allow it to reach an acceptable level of thermal stress, and reduce its density. Carbon fiber is an exciting candidate for this role because of its thermodynamic compatibility, high specific strength and hardness with ZrB_2-SiC below 3000 K, and high-temperature resistance above 2000 K [2].

Compared to conventional methods, the Spark Plasma Sintering (SPS) technique makes it possible to sinter ZrB_2-SiC composites at lower temperatures and in shorter times. In the SPS technique, while a direct current is applied to the powder-filled graphite die, a uniaxial pressure is applied to the die simultaneously. Thus, grain growth can be prevented thanks to the fast heating rate, and a denser microstructure can be achieved. In addition, the microstructure can be kept under control with the help of faster heating rates and shorter processing times [3].

Hu et al. reported the mechanical properties of carbon fiber reinforced SiC-ZrB_2 composites produced by infiltration, pre-infiltration and pyrolysis (PIP) methods using slurry prepared from polycarbosilane (PCS)/ZrB_2/divinyl benzene (DVB) [4]. This study found that carbon fiber increased fracture toughness and ZrB_2 matrix improved flexural strength above 1800°C.

Asl investigated the effects of sintering conditions of SiC particles and chopped carbon fibers on the microstruc-

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Table 1. Materials used in ceramic slurry

Sample	Liquid Medium	Ceramic Powders	Dispersant	Binder
Set 1	Ethanol	Alpha-SiC and ZrB_2	PEI (~0,2 g)	PVB (0,1 g)

Table 2. Sintering parameters of the composites

Sample	Pressure (P_1)	Temperature (T_1)	Dwell Time (t_1)	Pressure (P_2)	Temperature (T_2)	Dwell Time (t_2)
Set1-1900-10min	50 MPa	1900 °C	10 min	-	-	-
Set1-1950-10min	50 MPa	1950 °C	10 min	-	-	-
Set1-2000-10min	50 MPa	2000 °C	10 min	-	-	-
Set1-1900-double-10min	30 MPa	1600 °C	5 min	50 MPa	1900 °C	10 min
Set1-1900-double-10min-PVB	30 MPa	1600 °C	5 min	50 MPa	1900 °C	10 min

ture and mechanical properties of ZrB_2-based composites. Asl reported that the sintering temperature was the most influential factor in hardness. In addition, the optimum production conditions were determined as 1850°C temperature, 6 minutes waiting time and 30 MPa pressure [5].

Balak et al. used Taguchi L_{32} experimental design to optimize the flexural strength of ZrB2-based composites prepared with SPS. As a result of this study concluded that the most critical effect on flexural strength was related to temperature, SiC and carbon fiber, respectively [6].

Karimirad et al. investigated the effects of short carbon fibers on the sinterability, flexural strength, fracture toughness and thermal shock resistance of spark plasma sintered ZrB_2-SiC composites. They found that the addition of short carbon fibers to the ZrB_2 – 30 vol.% SiC composite results in lower hardness, lower relative density, poor sinterability and increased volume percentage of open porosity [7].

This study focused on investigating the effects of sintering temperature, sintering step and binder use on the structural and mechanical properties of carbon fiber reinforced ZrB_2-SiC ceramic matrix composites. As far as we know, there is no other study in the literature investigating these three parameters simultaneously. In addition, the way the prepared slurry is applied to the carbon fiber fabric is one of the original values of the study.

2. Materials and Method

2.1. Preparation of ceramic slurry

The first step for the fabrication of composite materials is the preparation of ceramic slurries. In this study, ceramic slurries with 20 wt.% solids were prepared. The precursor powders used while preparing the slurry are alpha-SiC (Alpha Aesar, 2 microns, 99.8% purity) and ZrB_2 (H.C. Starck, Grade A). In addition, polyethyleneimine (PEI) was used as a dispersant and polyvinyl butyral (PVB) was used as a binder. Ethanol was used as the liquid medium. The SiC ratio in these powders was 20%wt. Moreover, the effects of binders were examined while preparing some materials. These materials are from now on referred to as Set 1.

Ceramic slurries were prepared using separate plastic bottles for each sample. Starting materials were added to the plastic bottles indicated in Table 1. Si_3N_4 balls were placed in each bottle to obtain a more homogeneous mixture and the slurries were mixed for 24 hours in a ball mill. The amount of slurry prepared for each composite is approximately 50 ml.

After the ceramic slurry was prepared, this slurry was impregnated with carbon fiber fabrics. Firstly, carbon fiber fabrics were cut in a circular shape, arranged in a single layer, and pour the slurry on them. Circular fabrics had a diameter of 4 cm. 24 layers of carbon fiber fabrics were used for each sample. Circular fabrics were left in an oven for 24 hours to evaporate the alcohol and dried completely.

2.2. Sintering of materials with the spark plasma method (SPS)

Graphite dies with a diameter of 40 mm were used in Spark Plasma Sintering (SPS). First, the graphite die's lateral, upper and lower surfaces were covered with graphite foil. Then, the fabrics were placed in a graphite die. In this study, some samples were subjected to single-stage and double-stage sintering processes, and these processes' effects were discussed. The applied pressure, maximum temperature and dwell time in the single-stage sintering process were expressed as P_1, T_1 and t_1, respectively. In

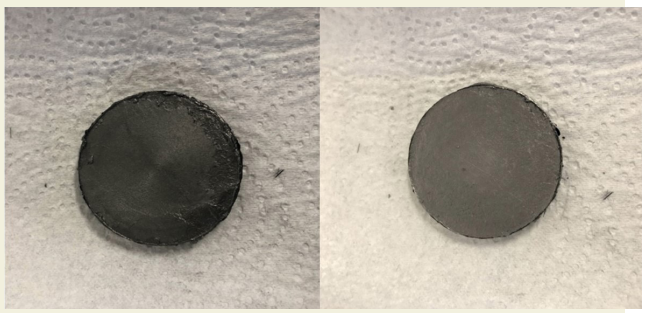

Figure 1. Images of composite materials obtained after the sintering process.

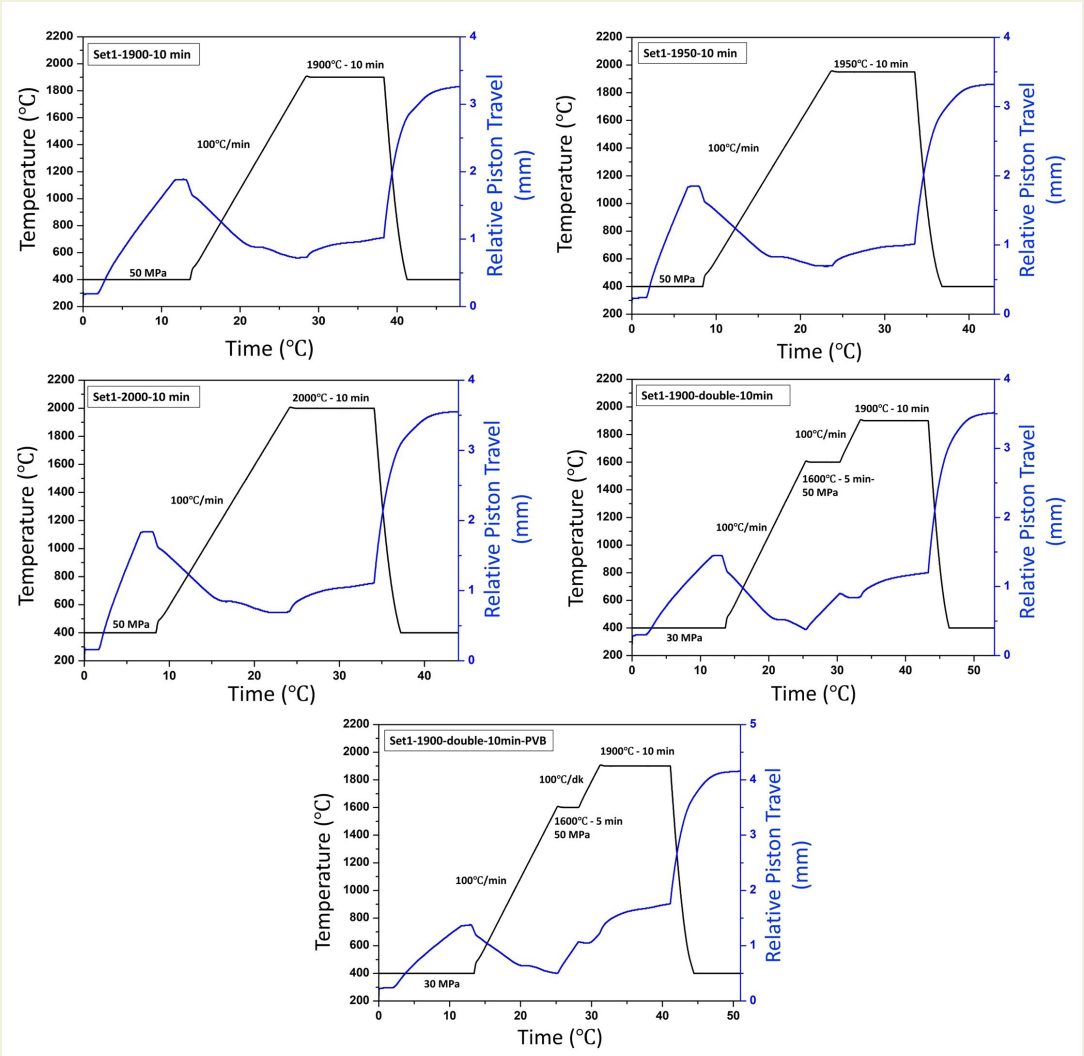

Figure 2. SPS curves of Set-1 samples.

double-stage sintering, the first pressure, temperature and dwell time are P_1, T_1 and t_1, respectively, and then the applied pressure, maximum temperature and dwell time in the second stage are indicated as P_2, T_2 and t_2, respectively. Table 2 shows the sintering parameters of samples with different compositions. Some of the samples obtained after sintering are shown in Figure 1. The diameter of the samples obtained after the sintering process was 4 cm and their thickness was approximately 3.5 mm.

Figure 2 shows the SPS curves of the composites. Set-1 samples were subjected to two different sintering processes as single-stage and double-stage sintering. In single-stage sintering, the applied pressure was chosen as 50 MPa, the heating rate was 100 °C/min, and the dwell time was 10 minutes. To determine the most suitable sintering temperature of the samples with the same composition, experiments were carried out at three different temperatures, 1900 °C, 1950 °C and 2000 °C. As seen from the sintering curves, sintering could not be fully realized at all three temperatures. Due to the incomplete sintering, sintering was carried out for two samples with and without binder additives having the same composition. This time, double-stage sintering was applied instead of single-stage sintering. When the single stage sintering graphs were examined, it was decided to perform double-stage sintering by waiting at 1600 °C due to the change in the relative piston travel observed at approximately this tempetature. The reason for this is to observe whether there will be an increase in density with double-stage sintering compared to single-stage sintering.

When the sintering graphs of these samples were examined, it was seen that the sample had started to sinter but a fully sintered structure could not be obtained because the temperature and/or time were insufficient.

After the sintering process, the surface of the samples was removed from the graphite foil. Samples were kept in the oven for a while and the moisture in the samples was removed. Dry weights of the moisture-removed samples were measured and recorded. Then, for density measurements, the samples were taken into separate beakers and boiled in distilled water for 120 minutes, and wet and air weights were measured using the Archimedes kit. Density calculations were made according to these values. Then

the samples were cut into suitable sizes for mechanical tests, microstructure and phase analysis.

3. Results and Discussions

3.1. Density analysis

The Archimedes method calculated the produced composites' densities and open porosity values with the following equations [8].

$$d = \frac{W_3}{W_2 - W_1} \quad (1)$$

$$O.P(\%) = \frac{W_2 - W_3}{W_2 - W_1} * 100 \quad (2)$$

Here, d is the composite density, W_1, W_2 and W_3 are air, wet and dry weights, respectively. The results obtained from the density calculations are given in Table 3.

When the results of the density analyzes of Set-1 samples were examined, it was observed that the density values of the samples increased as the sintering temperature increased in the samples with single-stage sintering, as expected. When the single and double-stage sintered samples were compared, it was seen that the density values of the samples sintered in single and double stages at the same time were quite close to each other. When the samples with and without binder added were compared with each other, it was seen that the highest density value belonged to the sample subjected to a double-stage sintering process at 1900 °C and to which binder (PVB) was added.

3.2. Phase development

The X-Ray Diffraction (XRD) method was performed for phase analysis of the composites. Rigaku Miniflex XRD machine was used for these analyses. Firstly, XRD analyses were performed to determine any impurities in the starting powders: alpha-SiC and ZrB_2. Figure 3 shows the XRD patterns of these powders. No secondary phase was found in the XRD patterns of the starting powders.

XRD patterns of Set-1 samples were given in Figure 4. The sample content is carbon fiber fabric, ZrB_2 and SiC powders. These phases were found in the structure. Due to the carbon fiber fabric and the graphite die used during sintering, it was seen that carbon and graphite phases were also included in the structure. Finally, in addition to these phases, the ZrC phase was also found in the structure. This ZrC phase was also encountered in another study [9], and it was reported that this was due to the reaction between covering the ZrB_2 particles ZrO_2 and C, according to the following reaction:

$$ZrO_2 + 3C = ZrC + 2CO \quad (3)$$

The formation of these phases has also been revealed in previously reported studies [10-13].

3.3. Microstructure analysis

Scanning electron microscopy (SEM) images of Set-1 samples are shown in Figure 5.

When the microstructures of Set-1 samples were examined, it was seen that the composite (Set1-1900-double-

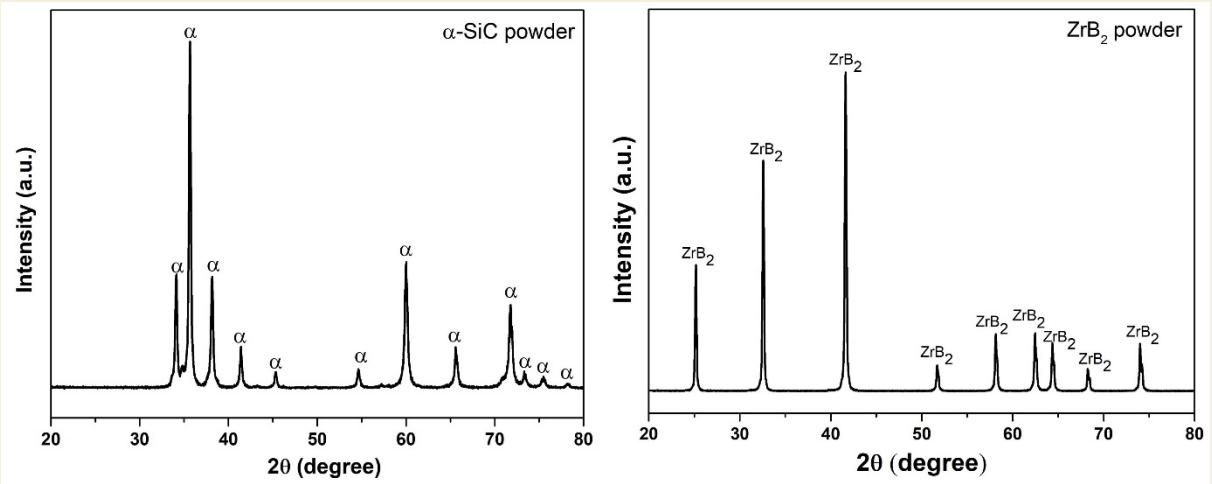

Figure 3. XRD patterns of (a) alpha-SiC and (b) ZrB_2 powders,respectively.

Table 3. Density and open porosity values

Sample	W_1 (g)	W_2 (g)	W_3 (g)	Density (g/cm³)	O.P (%)
Set1-1900-10min	3,408	7,0286	6,4951	1,7939	14,74
Set1-1950-10min	3,126	6,321	5,9605	1,8656	11,28
Set1-2000-10min	3,2953	6,5375	6,0898	1,8783	13,81
Set1-1900-double-10min	3,1518	6,5679	6,1335	1,7955	12,72
Set1-1900-double-10min-PVB	5,2399	9,0005	8,6905	2,3109	8,24

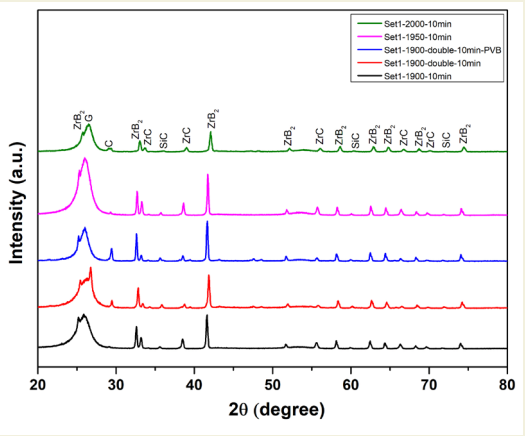

Figure 4. XRD patterns of Set1-samples.

10min-PVB) produced with a slurry-containing binder had the densest structure. This result is also consistent with the density analyses determined by Archimedes' principle, as mentioned in the previous section. It is thought that the reason is that the binder (PVB) stabilized the viscosity of the slurry [14].

As can be seen from the microstructures of composites, it is seen that the densification is higher in composites containing binder (PVB). However, as can be seen from the images, it was also observed that a homogeneous density could not be obtained throughout the entire structure and the ceramic particles were not fully homogeneously distributed between the fibers. Moreover, despite dense regions in places, there is still regional porosity between the fibers.

3.4. Mechanical properties

The mechanical properties of the composites were investigated using the three-point bending test. Instron 5581 device was used for this test. Measurements were carried out at room temperature. The dimensions of the test specimen were approximately 3 mm x 4 mm x 25 mm. The applied force was 2 kN with a span of 20 mm and a cross-head speed of 0.5 mm/min. Three-point bending test results of Set-1 composites are shown in Table 4.

Compared to similar studies, the mechanical results of our samples were found to be approximately two to one-third lower than the results reported in the literature [15-16]. It is thought that this is due to the inability to obtain a dense structure throughout the entire composite, as clearly determined from both density analyses and microstructure images, due to insufficient sintering temperature or time.

Hu et al. reported a decrease in flexural strength and

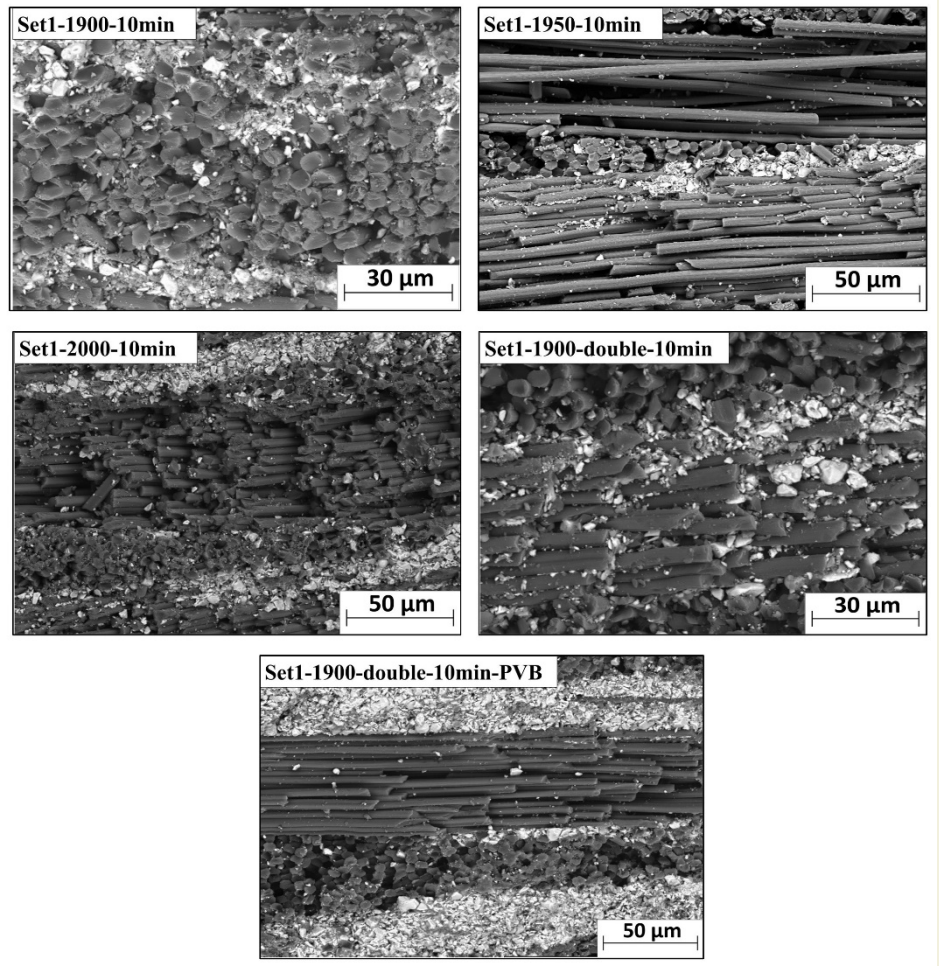

Figure 5. SEM images of Set-1 samples.

Table 4. Mechanical test results of Set-1 composites.

Sample	Maximum Flexure load (kN)	Flexure stress at Maximum Flexure load (MPa)	Modulus (Automatic) (GPa)	Flexure strain at Break (Standard) (mm/mm)	Flexure extension at Maximum Flexure load (mm)	Flexure stress at Break (Standard) (MPa)
Set1-1900-10min	0.039	30.244	4.87	0.17697	0.34032	8.37630
Set1-1950-10min	0.050	36.134	5.97	0.08409	0.34214	10.15255
Set1-2000-10min	0.039	22.196	1.96	0.12573	1.62585	7.05098
Set1-1900-double-10min	0.029	19.101	2.46	0.10869	0.31020	6.15574
Set1-1900-double-10min-PVB	0.071	54.954	11.93	0.15320	1.54052	11.25895

modulus with increasing the amount of ZrB_2 in the structure. In the same study, it is stated that the presence of carbon fiber contributes to both flexural strength and elastic modulus. Carbon fiber significantly increases flexural strength, which provides excellent thermal shock resistance under ultra-high temperature conditions, while increasing the reliability ratio of composite materials, enabling the production of thicker and more complex materials [4].

4. Conclusions

In this study, composites were fabricated under different sintering conditions using alpha-SiC, ZrB_2 starting powders and carbon fiber fabric, and the effects of these conditions on density, microstructure, phase analysis and mechanical properties were investigated. In addition, the impact of using binders in producing some materials was characterized. If the results obtained are summarized;

- The highest density was reached in Set1-1900-double-10min-PVB composite, which was sintered in double stages and contained a binder. It is thought that the double-stage sintering process has a positive effect on the densification mechanism.
- Consistent with the results obtained from the density analyses, it was also found that the samples sintered in double-stage and containing binder exhibited a denser microstructure.
- It was determined that the material with the best mechanical properties was Set1-1900-double-10min-PVB. It is thought that using PVB as a binder in this material improves mechanical properties.

5. Acknowledgement

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