



In-situ syhnthesis of $\text{SiC-ZrC-Al}_2\text{O}_3\text{-ZrO}_2$ composite

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ABSTRACT

Purpose: The aim of the study was the processing of SiC based ceramic of $\text{SiC-Al}_2\text{O}_3\text{-ZrO}_2$ composite with the various of starting composition silicon carbide (from 20% to 60 %), zircon (from 20% to 60%) and aluminum (from 0% to 10%) powders using solid and liquid sintering methods, and the physical properties and the characterization of the newly formed phases ant used experimental parameters.

Design/methodology/approach: In order to analyses the reaction mechanism as well as the thermal behavior of the starting compositions, thermal analysis /TG/DTA and for the determination of nay phases, X-ray diffraction methods were used. To examine the morphology and particles morphology and the microstructures, scanning electron microspore (SEM) was used.

Findings: The TG/DTA curves show endo/exothermic peaks related with the formation of carbides. The addition of Al was prevented the formation of yttrium aluminates phases. In presence of Al, the reduction and the liquid phase formation takes place. SiC acts as reducing agent. $\text{SiC-Al}_2\text{O}_3\text{-YSZ-ZrO}_2$ phases were detected but at higher temperature the reaction phases were changed to ZrC, AlYzr, Y_2O_3 were detected as major phases in the processed samples.

Practical implications: After the determination of the obtained phases, the resulting product is ceramic composite which consists of $\text{SiC-Al}_2\text{O}_3\text{-YSZ-ZrO}_2$, ZrC, AlYzr, Y_2O_3 phases. It has potentially attractive composite where requires thermal stability in high temperature applications.

Originality/value: The addition of aluminum to the mixture was facilitate the sintering process, was lowering the sintering temperature due to the high exothermic reaction which changes the reaction mechanism of the sintering from solid to liquid one.

Keywords: Ceramics; Composite; Liquid phase sintering; SiC based ceramics

Reference to this paper should be given in the following way:

A. Atasoy, In-situ syhnthesis of $\text{SiC-ZrC-Al}_2\text{O}_3\text{-ZrO}_2$ composite, Archives of Materials Science and Engineering 78/2 (2016) 53-58.

MATERIALS

1. Introduction

Silicon carbide is one of the most important covalently bonded compounds that exhibit many interesting and attractive materials properties [1]. It is well known, one of the hardness materials after the diamond and boron compounds. Aside the hardness property, SiC has many other excellent properties including high strength and creep resistance at high temperature, low bulk density, good thermal, electrical, chemical, nuclear properties high thermal conductivity, low nuclear activation, high thermal shock resistance, high electrical field strength, high oxidation and chemical resistance [1-3]. As a result of these unique properties, SiC is used to many hard environments in mechanical and structural applications. They are cutting tools, heat exchangers, gas turbines, thermal barrier coating, high reflective material, heating elements, coating layer around nuclear fuels in high temperature reactors [1].

SiC is used alone or in combination of different metals or oxide in many applications. There are large number of manufacturing method of the silicon carbide based materials which are solid state sintering [4,5], liquid phase sintering [6,7], hot pressing [8], spark plasma sintering[9]. Pure silicon carbide is difficult to be sintered in the solid state sintering process even at high temperature because of its inner strong covalent bond. It is conventionally sintered with small amount of sintering aids such as Al, B, C which is increased densification of SiC. To lower sintering temperature and improve mechanical properties of the silicon carbide different additives were introduced to it. With addition of various oxide groups, such as Al_2O_3 - SiO_2 , AlN - Y_2O_3 , Al_2O_3 - Y_2O_3 or Al_2O_3 - Y_2O_3 - MgO were provided a liquid phase which is called liquid phase sintering of SiC which was resulted a new phases such as rare earth aluminates or oxynitrides [10-13]. The process facilitates sintering and densification of SiC, depends on the second phase in the SiC mixture and the liquid phase sintered samples have better mechanical properties than the solid state sintered samples. It was reported that, the incorporation of a dispersion of second phase with lower thermal coefficient than the matrix can improve the mechanical properties of ceramics [14]. It has been also reported that small amount of sintering aids like ZrO_2 [15], B_2O_3 [16,17], Y_2O_3 [18,19], MgO [20] were added to composite to increase densification and sinterability of composite. It was reported that, addition of ZrO_2 was improved the thermo mechanical properties of the ceramic matrix leading to toughness by transformation and micro cracking [21].

As mentioned above, SiC based ceramic composites have been fabricated by mixing of silicon carbide with

different metals or oxides. In the present work, SiC - Al_2O_3 - ZrO_2 ceramic composite were in-situ fabricated by reaction sintering of SiC - Al_2O_3 and YSZ powder with addition of small amount of Al powder. The results were given and discussed in the following part of the work.

2. Experimental

SiC , α - Al_2O_3 , YSZ and Al powders were blended with 6 different ratios which were presented in Table 1.

Table 1.

The used composition and the experimental parameters

Series	SiC	YSZ	Al_2O_3	Al	Sintering temp. 1300-1500°C	
S5	40	40	20	0	2h.	4 h.
S6	40	40	15	5	2 h.	4 h.
S7	60	20	15	5	2 h.	4 h.
S8	30	30	30	10	2 h.	4 h.
S9	20	60	15	5	2 h.	4 h.
S10	20	60	20	10	2 h.	4 h.

After the adding of pressing aid %1.5 PVA to the mixture of SiC - Al_2O_3 -YSZ-Al powder, the mixture was compacted to green bodies. The compacted samples were placed into SiC powder in a graphite crucible and then sintered at 1300 and 1500°C for different holding times in Ar atmosphere. The density and apparent porosity of the sintered compacts were determined using the standard water absorption method.

3. Results and discussions

3.1. Preparation mixtures

The selected XRD patterns of the starting composition are given in Figures 1a and b. It is clear that, there is no background noise giving the baseline as a straight line and there are no unknown peaks in the starting compositions. As seen from it, the major and minor peaks are SiC, Al_2O_3 , YSZ, ZrO_2 and Al phases. When comparing XRD peaks with or without Al powder addition, it is evident that there are some differences in number of peaks and their related intensities between Figures 1a and b. Sample 5 does not contain any metallic aluminium peak, in Figure 1b.

A scanning electron microscope samples (S5, 8, 10) shown in Figure 2.

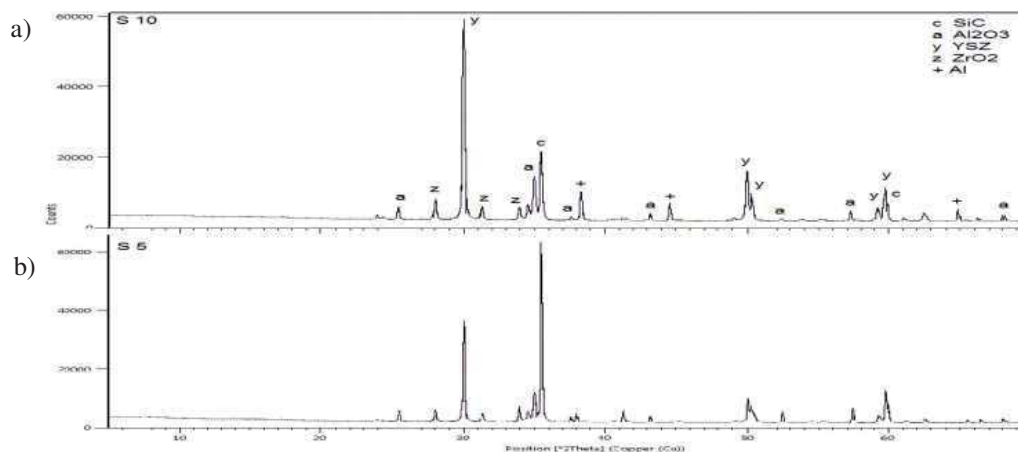


Fig. 1. X-ray diffraction patterns of the selected starting samples

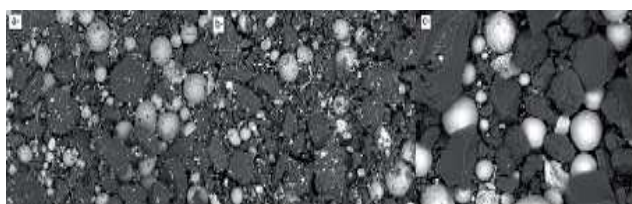


Fig. 2. Scanning electron microscope of the samples (S5, 8, 10)

Thermogravimetry provides a continuous measurement of any mass loss or gain with time at a fixed temperature and thereby give a complete picture of the starting composition. TG curve of the starting composition of the SiC, Al₂O₃, YSZ and Al powders at temperature between 25-1500°C was presented in Figure 3. There is significance change in mass of the mixture, during TG experiment. As seen from the curve, it can be divided into 6 steps, according to the slope of the TG curve. As seen from it, up to 400°C is the first step occurred very small mass loss related with the moisture content of the mixture. The second step is between 300-400°C, a very fast and sharp mass loss occurs. The third step is steady state of the mixture at temperatures between 400- 800°C. The fourth step starts around 850°C up to 1050°C. At this stage, the sample shows a mass gain behaviour. The speed of the mass gaining process is slow down at temperatures between 1050-1200°C which represents the fifth step of the TG. When the mass gain accelerated at 1200°C, the final step was started. According to the mass of the Sample 8, TG curve can be divided into two stages are the losing and the gaining stages. Up to 450°C it is the mass loss stage and the mass gaining stage starts at 450°C to 1500°C. At the mass loss stage, there is fast and sharp decrease in

the mass of the sample was around 1.5%. In the second stage, the total mass gaining was around 5%. It was assumed that there is linear relationship between the mass loose of the mixture with the reduction of the oxide content and as well as the mass gaining of the sample with the formation of carbide in the processed sample.

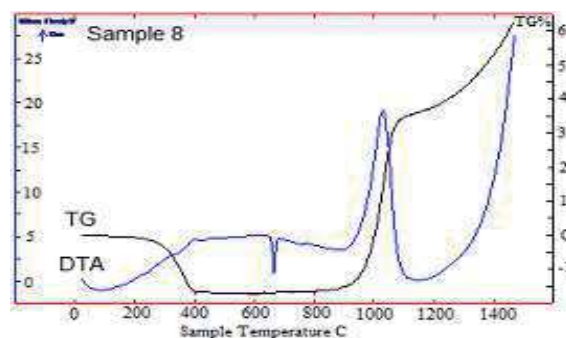


Fig. 3. TG/DTA curves of the mixture of SiC, YSZ, Al₂O₃ and Al powders (S8)

Figure 3 shows the DTA curve of the sample 8. There is one endothermic peak at around 650°C can be associated with the melting point of aluminium content in the sample. Besides of it, The DTA curve of the sample 8 shows two exothermic peaks at temperatures 1000 and 1450°C. The first exothermic peak is most likely to be related with the aluminothermic reduction of an oxide in the sample. The second exothermic peaks can be seen from the curve that it is uncompleted peak at above 1450°C which is likely to be related with any decomposition of SiC and formation of new carbide phases, such as ZrC, during the sintering. The decomposition of SiC is feasible depending on oxygen availability of the reaction atmosphere and temperature.

Under the experimental conditions, the oxygen source is only the oxide in the starting composition. The reduction of the oxide in the sample is also possible by aluminothermic and by SiC reactions during the processing.



3.2. Characterisation of the sintered samples

The X-ray diffraction patterns of the reduced samples are presented in Figures 4-6 for sintering carried out for 2 and 4 hours from 1300°C to 1500°C in presence of static air and nitrogen atmospheres.

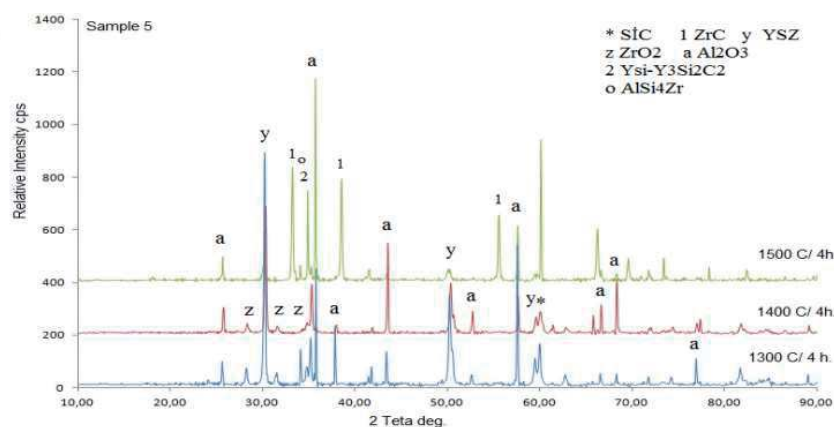


Fig. 4. X-ray diffraction pattern of the reduced sample 5 at 1300-1500°C for 4h

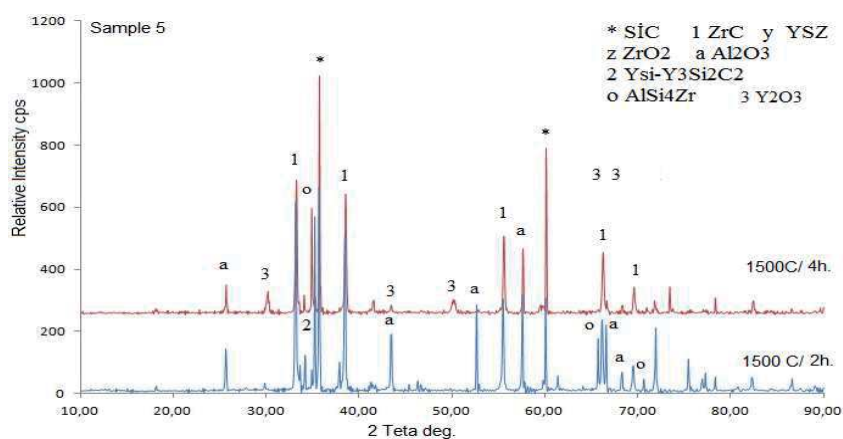


Fig. 5. X-ray diffraction pattern of the sintered sample 5 at 1500°C for 2 and 4h

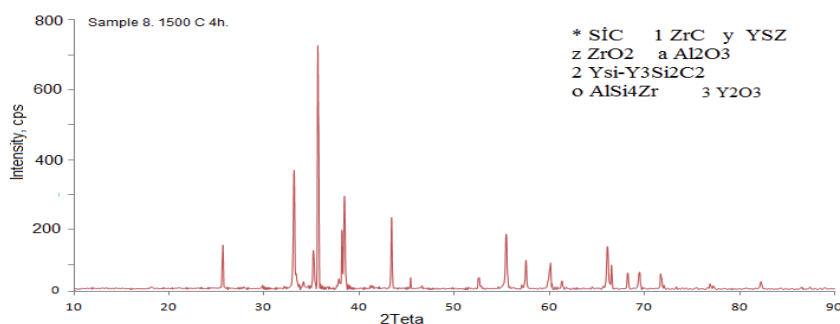


Fig. 6. X-ray diffraction pattern of the sintered sample 8 at 1500°C for 4h

In Figure 4, depending on the reaction temperature there are huge differences in phases and changes in the intensities of peaks. At 1300°C for 4h holding time, YSZ was the dominant, Al₂O₃ and SiC are the second major phases, ZrO₂ was the third phase in the reduced sample 5.

No other phases were detected in it. When the reaction temperature increased to 1400°C for same holding time, approximately there were no phase change in the sample but the intensities of the peaks were changed. When the reaction temperature increased to 1500°C under the same conditions, there was formation of new phase.

Figure 5 represents the X-ray diffraction pattern of the reduced sample 5 at 1500°C for various holding times. As seen from it, there are some differences in the intensities of the peaks as well the formed phases in the sample 5. When the reaction time increased to 4h, some peaks were disappeared or resulted large peaks. The detected phases for both holding times were labelled on the XRD patterns.

Figure 6 shows the X-ray diffraction patterns of the reduced different starting compositions (Sample 5 and Sample 8) at 1500°C. It is clear that, the patterns were on different forms. There were huge differences between two patterns in terms of the phases and intensities. When the reaction time increased to 4h, some peaks were disappeared or resulted large peaks. All the peaks were identified and labelled on the XRD patterns.

As seen XRD patterns of the reduced samples, depending on the starting compositions, the reaction temperatures and holding times, there are huge differences in phases and changes in the intensities of peaks after the sintering operations. When comparison of the starting phases with the reduced samples, some phases were disappeared at higher reaction temperatures. As seen from Figures 1a and b, SiC, Al₂O₃, YSZ and Al phases identified and labelled on it.

3.3. Analysis of the morphology

Scanning electron micrograph of the reduced powders was presented in Figure 7. When comparison of the starting mixtures images with the reduced samples, there were big differences between the samples. It was assumed that larger particles and agglomeration were obtained as a result of the liquid phase.

To understand, the sintering mechanism of the SiC-Al₂O₃-YSZ system with or without addition of Al powder, a series of experimental works were carried out. Depending on the starting composition, reaction time and temperature the formation of the phases were changed. At temperature 1300°C, the formation of AlSiZr was detected in the XRD. The YSZ phase was disappeared at higher reaction temperatures. The formation of ZrC phase was detected at 1500°C.

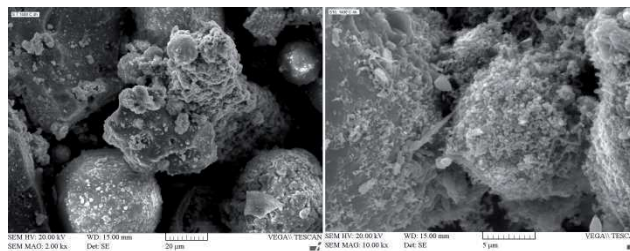


Fig. 7. Scanning electron images of the sintered samples

In the SiC-Al₂O₃-YSZ-Al system, it was assumed that the process was involved in three stages where is the melting of aluminium powder takes place at around 660°C, the reduction of the oxide by aluminothermic and finally the decomposition SiC and the formation of new carbide phase of ZrC. One of the advantages of the process is the changing of reaction state from solid-solid to solid-liquid. Another important feature of the process is the heat requirements for the formation of new phases, such as ZrC. Since the aluminothermic process generates large amount of heat, SiC gives the second exothermic reaction in the system. The process changes the reaction mechanism and creates an interface between liquid metal and solid parts of the mixture during the sintering and the wettability of each one determines the rate of the sintering process.

As seen from the XRD and TG/DTA figures, with addition of metallic Al to the mixture, the aluminothermic process was feasible and starts at temperature above 1050°C resulted an exothermic reaction in the samples. YSZ decomposes at temperature above 1300°C and the YSZ content of the samples was successfully decomposed at higher temperature and ZrC phase was detected at 1500°C. It is also clear from the results that; the second exothermic reaction was related with SiC acts as a reducing agent above 1450°C.

4. Conclusions

In the presence of SiC-Al₂O₃-YSZ, the final composite powder was formed by the direction of decomposition behaviour of the YSZ and the carbide phases in the system. Without any addition to the mixture, the carbide phase decomposes at temperature above 1450°C which depends on the sintering atmosphere. In another words, SiC acts as a reducing the oxide content in the sample and depending on oxygen potential it oxides above this temperature.

In the presence of metallic aluminium powder the mixture of SiC-Al₂O₃-YSZ powders, the reaction mechanism of the sample was totally altered. There were liquid phase formation as a result of the aluminothermic and the decomposition of SiC in the samples. It was

suggested that the addition of Al created the second exothermic reaction in it. As a result of the two exothermic reactions, the huge amount of heat generated in the sintering operation. At lower reaction temperature, SiC-Al₂O₃-YSZ-ZrO₂ phases were detected but at higher temperature the reaction phases were changed to ZrC, AlY₂Zr, Y₂O₃ were detected as major phases in the processed samples. Besides of these phases, any YAG, YAM or YAP phases were not detected in the products. This can be explained the complexity of the oxides and the carbides in the starting compositions or as explained above the addition of Al was prevented the formation of yttrium aluminates. As a conclusion, the depending on the reaction temperature and the starting compositions, SiC-Al₂O₃-ZrO₂/ZrC composite was obtained under the experimental conditions. The mechanical properties and microstructure parts is going to be presented in another work.

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