Densification and characterization of SiC-AlN composites for solar energy applications

Dina H.A. Besisa [a, c], Emad M.M. Ewais [a, *], Yasser M.Z. Ahmed [a], Fouad I. Elhosiny [b], Denis V. Kuznetsov [c], Thomas Fend [d]

[a] Refractory & Ceramic Materials Division (RCMD), Central Metallurgical R&D Institute (CMRDI), P.O. Box 87 Helwan, 11421 Cairo, Egypt
[b] Chemistry Department, Faculty of Science, AinShams University, Cairo, Egypt
[c] Functional Nanosystems and High-Temperature Materials Department, National University of Science and Technologies "MISiS", Leninskiy Pr. 4, 119049, Moscow, Russia
[d] German Aerospace Center — Linder Höhe, 51147 Köln, Germany

ARTICLE INFO

ABSTRACT

In an attempt to solve one of the most critical global concerns of energy resources depletion, the present work is focused on tailoring and processing of a new volumetric receiver material for solar energy and high temperature applications. This in turn support producing a highly qualified solar receiver material for the future energy and electricity supply of Middle East and Europe. Herein, the processing and studying of the different parameters affecting on the preparation of near fully dense SiC/AlN structures and investigation of their different characteristics were achieved. These ceramic composites will constitute the final foam struts of the pores of the volumetric air receiver. Various SiC/AlN composites were designed with different ratio of AlN content (0—40%) and produced via pressureless sintering. Influence of different parameters on sintering and densification of SiC/AlN composites such as sintering atmosphere, additives and temperature were investigated in order to achieve the required and qualified properties of the final product of proposed SiC/AlN solar receiver. The quality and performance of the produced composites were evaluated and analyzed through different investigations, including XRD, densification parameters, microstructure examination and thermal properties. The results show that the best sintering conditions for producing a highly dense and qualified carbide/nitride receiver was attained at a temperature of 2080 °C in argon/vacuum with 2.5%Y + A addition. The characteristics of the investigated composites were mainly dependent on their densification behavior and AlN content. Thermal conductivity, diffusivity and coefficient of thermal expansion gave enhanced values at high temperatures. The inspected SiC/AlN composites can be strongly nominated to be used in solar energy applications.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Solar tower technology is the future predictable way for the generation of large amounts of electricity from concentrated solar radiation in high solar resources countries such as North Africa and the Middle East, India, Australia, North and South America, countries known to belong to the so called "sun-belt" of the earth. Solar thermal systems are becoming an attractive alternative to reduce the environmental impacts. These systems are clean and require no fossil fuel. Another advantage of this technology compared to other technologies is its availability. The total solar energy flux intercepted by the earth on any particular day is $6.26*10^{20}$ J per hour. This is equivalent to burning 360 billion tons of oil (toe) per day or 15 Billion toes per hour [1].

The major element of the solar tower technology is called, the open volumetric solar receiver. It consists of a porous material that is heated by the concentrated solar radiation to high temperature and is used to feed a conventional steam turbine process. The concentrated solar radiation is generated by a large number of controlled mirrors (heliostats), each of which concentrate and re-directs the solar radiation onto the receiver as a common target on

the top of a tower. Here at the focal point the so called solar air receiver is located, which absorbs the radiation and converts it into high temperature heat. Porous high temperature resistant materials are used as receivers. As a heat transfer medium air is used, which is heated up by flowing through the open cells of the hot receiver material and which then feed a conventional boiler of a steam turbine. The turning motion of the turbine is used to create electricity [2,3].

The first volumetric receiver experiments were investigated in the late seventies by SANDERS Assoc. Company and the Battelle Pacific Northwest Laboratory. The development of receiver system has been considered sufficiently mature since the demonstration plants built mostly during the 1980s and the wide variety of receivers tested to date [1,4]. Generally, volumetric receivers should have high efficiencies, high temperature resistance, and high absorptivity in the visible and near infrared range and has to be combined with a high porosity to create large surfaces for convective heat transfer from the solid absorber to the fluid [4—6]. However, in some cases, the absorbers tend to be sensitive to inhomogeneous flux distributions, which may cause local overheating of the material. This can be attributed to the increase of the viscosity of air with increasing temperature, so the permeability of the hot parts of the receiver became lower. In various tests with specific kinds of materials, flow instabilities occurred, which partly lead to hot spots and a sudden destruction of the receiver. To overcome this problem and achieve both high efficiencies and reliable operation, an optimized combination of thermal conductivity and heat transfer parameters has to be selected and optimized [6—8].

Ceramic materials have become of interest as volumetric air receivers. They are capable of producing high outlet air temperatures, which in turn enhance the system efficiency. Furthermore, there are other benefits of the ceramic absorber structures as that higher flux densities and gradients are possible, this enables a smaller receiver aperture, thereby lowering system costs and reduce radiation losses. In addition, their durability and lifetime can be extended owing to their aggressive characteristics. Non-oxide ceramics based on carbide/nitride materials are have been used as solutions to many severe material problems over the past 30—40 years due to their attractive characteristics and extended applications.

SiC ceramics have been long used successfully as solar volumetric solar receiver material. It has attractive properties for high temperature applications because of their high hardness, toughness, young's modulus, excellent absorption, excellent high temperature strength, high Seebeck coefficient, good electronic properties, high creep resistance and oxidation resistance and also has been expected as high temperature semiconductor with wide band gap. SiC also has a high figure of merit in high temperature range. However, the silicon carbide receiver still suffers from some disadvantages concerning limitations in its reliability and toughness in some aggressive applications [9]. We must also take into consideration the simplicity of the manufacturing to achieve low costs for the whole receiver system, which at least lowers the generation costs of energy and electricity.

Moreover, AlN ceramics owe unique characteristics such as high thermal conductivity, low thermal expansion coefficient, high thermal shock resistance, high corrosion and oxidation resistance, and mechanical strength. Due to the rare combination of properties, AlN is attractive for high temperature and refractory applications such as metal handling, in semiconductor devices, and as heat sinks, grinding media, seals, filler materials, Opto-electronics, dielectric layers in optical storage media, electronic substrates and chip carriers where high thermal conductivity is essential [10—12].

It was found that, combination of ceramic carbides and nitrides can create a new material with unparalleled properties that can enhance the performance of the receiver by combining the different characteristics of the two materials. Therefore the manufacturing of a new volumetric solar receiver from SiC and AlN ceramics can improve and enhance the performance of the receiver by combining their high temperature characteristics.

Furthermore, SiC and AlN could react and form an extensive complete solid solution due to their similar structure and high temperature properties which in turn can enhance their mechanical performance and durability [13—15].

SiC/AlN ceramic composites have many interesting applications, mainly in electronic: amplifiers (in traveling_wave tubes), klystrons, electronic instruments, and high temperature fields. Moreover, the electrical properties of AlN—SiC ceramics are expected to be beneficial and important for consideration in new applications, such as microwave absorption in high-power amplifiers and microwave components, sensor materials, thermoelectric conversion elements, and new wide bandgap materials. Furthermore, SiC/AlN thin film has been used to fabricate a wide variety of radio frequency resonators and filters for applications in telecommunication and sensing fields [16—19].

On the other side, some researchers have produced different SiC/AlN composites in order to enhance the characteristics of the two monolithic materials. Various methods and characterization for producing and evaluating these ceramic composites as chemical vapor deposition, hot pressing, plasma assisted gas source molecular beam epitaxy, spark plasma sintering and self-propagating combustion synthesis have been reported and investigated [20—25]. Ruh and Zangvil, have fabricated high density SiC/AlN composites from their powder mixtures by hot-pressing in the 1700″ to 2300 °C temperature range under vacuum atmosphere [21]. Chew et al., have explored the processing of AlN/SiC composites via polymer infiltration and pyrolysis of polymethylsilane (PIP) [26]. Influence of variations in processing conditions and additives on composite densification and microstructural development has been studied and analyzed. Kexin et al., introduced a new technique for producing AlN/SiC solid solution by combustion synthesis (CS) through ignition of the aluminium, silicon and carbon black mixtures under different nitrogen pressure values [27]. Hanning et al. investigated the preparation of SiC/AlN composite by the inorganic sol-gel processing from the mixture of silica sol, carbon black and alumina sol [28]. However, Production of carbide/nitride ceramics by these mentioned methods requires highly expensive starting materials or/and complicated apparatus. In contrast, from the industrial estimation, pressureless sintering is attractive, simple and cost effective method. However, not much work has been investigated on the pressureless sintering of SiC/AlN ceramics due to their poor sinterabilities. Since the cell struts of the pores of the volumetric air receiver are a key factor in the efficiency of the receiver, the determination and optimization of their characteristics are very important. Hence, the present work aims processing and studying the different parameters affecting on the preparation of near fully dense SiC/AlN structures constituting the final foam struts of the pores of the volumetric air receiver and investigation of their different characteristics. Different SiC/AlN composites are prepared with different ratios of AlN content (0—40%) by pressureless sintering. Influence of different parameters on sintering and densification of the different composites such as the effect of sintering atmosphere, additives and temperature were inspected. The quality and performance of the produced composites are evaluated and analyzed through different investigations, including XRD, densification parameters, microstructure examination and thermal properties.

2. 2- Materials and Experimental procedures

2.1. Raw materials and processing

High purity (99.99%) AlN, α-SiC and β-SiC (supplied by Hong Kong Tepu Refractory Co., Limited, China) were used as raw starting materials. To achieve a reasonable level of density, some highly pure and nano sized sintering additives as 2 wt% Y_2O_3 and 2.5 wt% $Y_2O_{3+}Al_2O_3$ were used. Different characterization has been carried out on these materials to identify their characteristics as XRD analysis, microstructure investigation FESEM &TEM and particle size distribution (PSZ) and surface area as showed in Figs. 1–8. The tailored mixtures of SiC/AlN composites without and with different content of sintering aid were prepared and given in Table 1.

Each composite mixture contained 50/50 wt% of β-SiC/α-SiC due to the high sinterability of β-SiC and the favorable combination of both α- and β-SiC at the same composite structure. In addition, ~ 5 wt % ortho phosphoric acid (H_3PO_4) was added to each mixture in order to protect AlN from hydrolysis and enhance its sinterability.

The different composites were mixed in 100% ethanol by planetary milling for 5 h (400 rpm). The obtained slurry was dried at 60 °C for 24 h then sieved. Green compacts of different SiC/AlN content were uniaxially cold pressed at 200 Mpa. The green compacts were covered with a powder mixture of 50% SiC:50% AlN as packing powder due to its efficiency in reducing the evaporation loss. Finally, different composites were pressureless sintered at high temperature graphite furnace under different sintering atmosphere (vacuum and argon/vacuum) and temperatures (1550–1750 and 2080 °C) with heating rate of 10 °C.
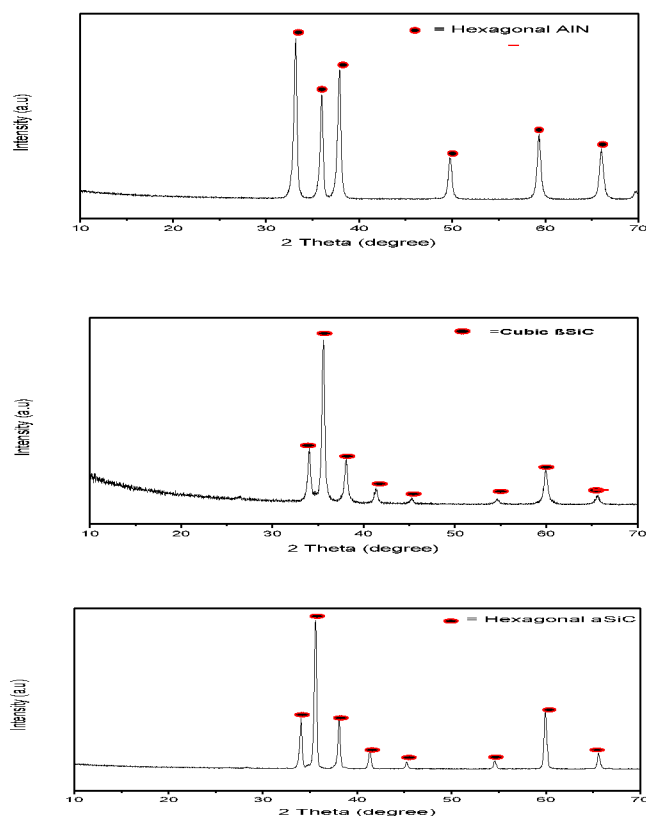

Fig. 1. XRD patterns of AlN, β-SiC and α-SiC raw powders.

2.2. Characterization

Particle size distribution of the starting materials was analyzed by laser diffraction using a Fritsch laser diffractometer (model Analysette 22 NanoTec). Prior to the measurement, the samples were accurately dispersed for 1 min of ultra-sonication using a 24 kHz Hielscher device (model UP 400S).

X-ray diffractometry was employed to monitor the formation of SiC/AlN solid solution, the degree of their solubility completion in each composite and to study the phase transformation behavior of SiC under different sintering conditions. XRD patterns of the raw materials and produced composites were characterized by a Brucker D8-advance X-ray powder diffractometer with Cu Ka radiation (k = 1.5406 Å).

Bulk density and apparent porosity of the sintered composites was obtained by Archimedes method. Relative density was estimated from the theoretical density of AlN (3.26 g/cm³), SiC (3.21 g/cm³), alumina (3.95 g/cm³), and yttria (5.03 g/cm³) in accordance to the rule of mixture.

The microstructural characterization was conducted to study the distribution of ceramic components in each composite, surface morphology and any other observed phenomena as phase transformation, liquid phase formation or grain growth. Powder morphology and microstructure of the different powders and composites were investigated by backscattered electron (BSE) in the field emission scanning electron microscopy(FESEM) using a Hitachi microscope (model TM-1000). In addition, high resolution transmission electron microscope (HR TEM; JEM- 2100, Japan) was used. TEM samples were prepared by dispersing the powders in acetone. Ultrasonic oscillation for 15 min was introduced to prevent the aggregation.

Thermal diffusivities of the produced SiC/AlN composites were evaluated by a NETZSCH-LFA 447 nano flash thermal analyzer through a temperature range of 298–573 K. The specific heats of composites were estimated by Setaram Labsys differential scanning calorimetry instrument under the protection of Ar gas over temperature 298–573 K. The density of the composites was determined by Archimedes' method. The thermal conductivity of the various composites was estimated from the following equation:

$$\lambda = C_p{}^* \, \alpha \, {}^* \, \rho \qquad (1)$$

where λ is the thermal conductivity (W/mK); cp is the specific heat (J/Kg.K); α is the thermal diffusivity (m²/s); and ρ is density (g/cm³).

Linear thermal expansion (LTE) and Coefficient of thermal expansion (CTE) are important properties that quantifies the volume change percentage in a material undergoes when it is subjected to temperature changes. They were performed by using **dilatometry (Model 402 C/1700, NETZSCH DIL., Germany).** In this measurement, specimens of diameter of 3 mm and a length of 12 mm are heated up to 1500 °C with a heating rate of 10° k/min in argon atmosphere with a flowing rate of 150 ml/min. LTE and CTE results were recorded by computer connected to dilatometer.

3. Results and discussion

3.1. Effect of sintering atmosphere

In order to form SiC-AlN solid solution, this system has to pass through three main steps. Initially, the AlN particle is vaporized from its own surface Next, AlN vapor is deposited onto the surface of the SiC grains and the AlN particle due to vaporization accompanied by a reduction in the size of it. Finally, the formation of partial SiC/AlN solid solution occurs at the boundary of the SiC grains [14]. The technical parameters which influence the solid
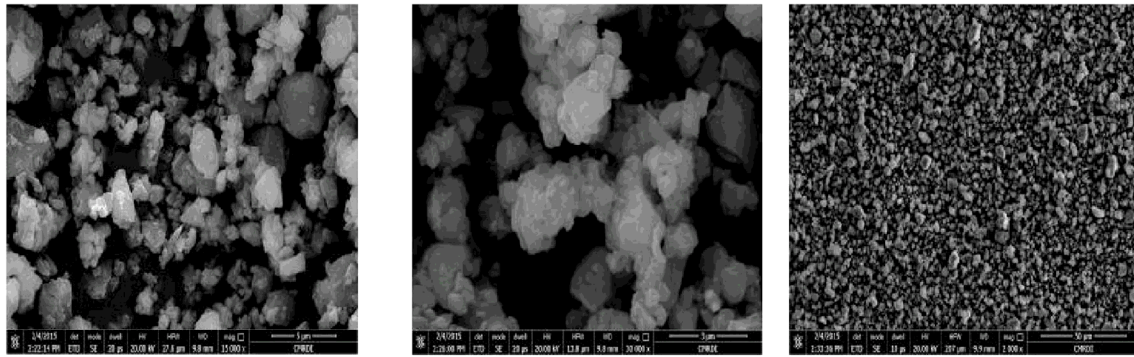
Fig. 2. FESEM of AlN powder.
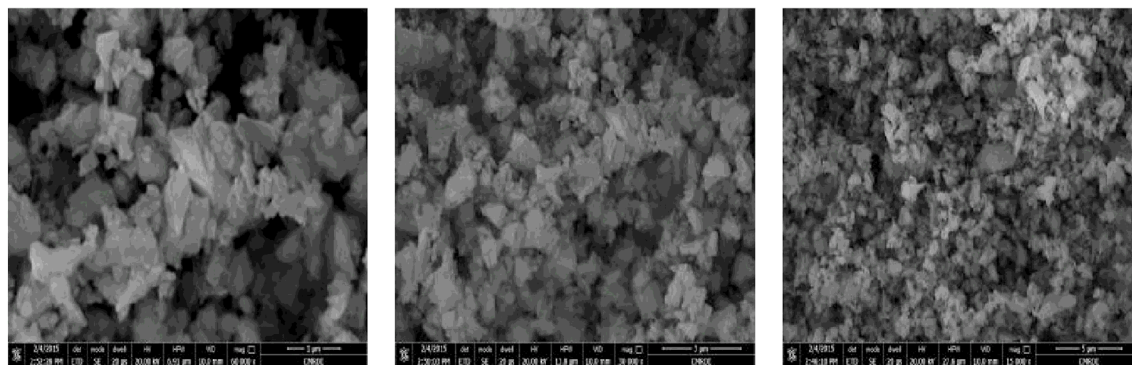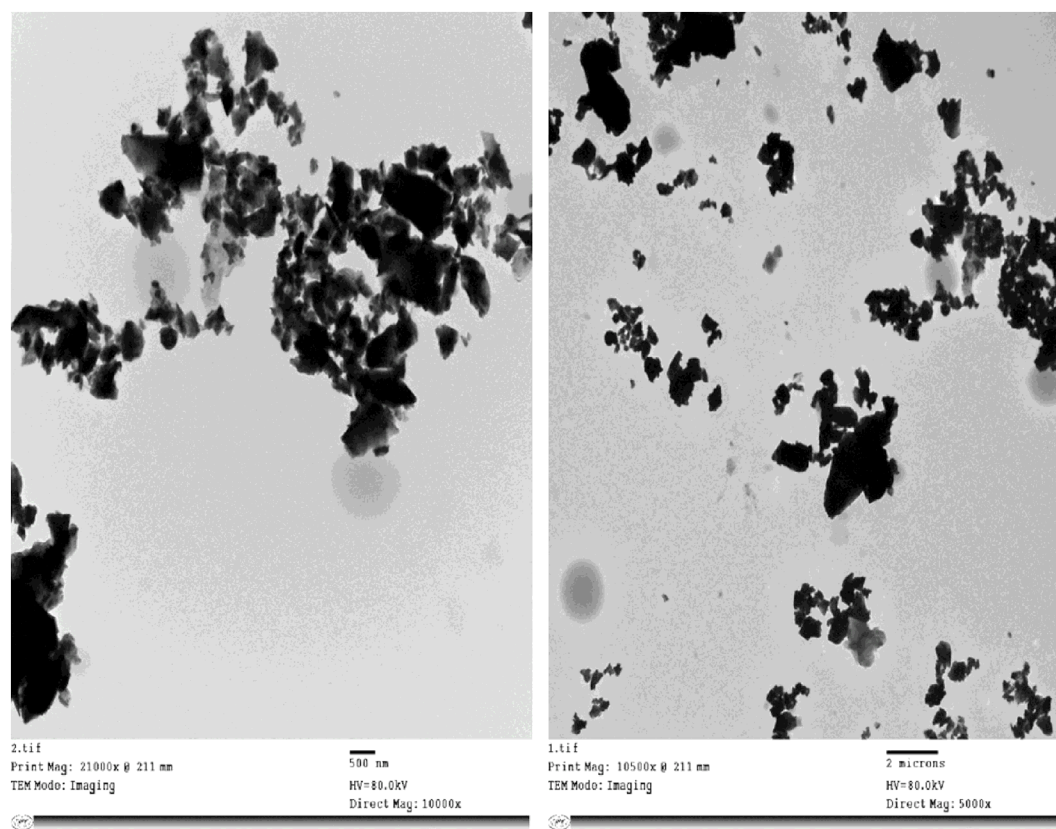

Fig. 3. TEM of AlN raw powder.

composites. This means that, the produced composites did not form a single phase and a complete solid solution under these sintering conditions. These results followed the SiC/AlN phase diagram presented by Zangvil and Ruh [21], Fig. 10. Moreover, the small peaks appeared at 2θ value of (≈26–29° & 48–50°) are belong to cristoballite (SiO$_2$) that reflect the oxidation of SiC and the none protected atmosphere which indeed observed from the surface of the sintered samples. Accordingly, highly pure argon gas with a pressure slightly higher than ambient atmosphere is used with the vacuum in the pressureless sintering of the different SiC/AlN composites in order to promote the performance of the sintering process and prevent the oxidation. Fig. 11 shows a comparison between the XRD pattern of sample 0X sintered at 1550° C/2 h in vacuum and Ar/vacuum atmospheres. It was found that, using Ar/vacuum atmosphere instead of vacuum only led to the formation of the required phases of AlN and SiC without any appearance of cristobalite or any other oxides.

On the other hand, bulk density, apparent porosity and relative density of the different sintered SiC/AlN composites (0X-4X) are measured and calculated in Table .2. Generally, it was found that with increasing AlN content, bulk and relative densities of SiC/AlN composites, increased and apparent porosity decreased. This can be attributed to that: AlN sinter more easily than SiC because the co-valences of SiC and AlN are 82% and 57%, respectively [29]. Therefore, the addition of AlN to SiC aids in the densification of the samples as compared with SiC alone, thus increasing the relative density and decreasing the porosity of the samples.

However, densities of the different SiC/AlN composites under these sintering conditions are still low. The maximum density of samples under these sintering conditions was only 1.94 g/cm^3, which is merely about 60% of the theoretical density. This behavior may be attributed to the sintering temperature, where it is not high enough to complete the solid solution reaction between AlN and SiC to increase the density. This situation can be solved either by using sintering additives or/and by increasing sintering temperature.

3.2. Effect of sintering additives and temperature

Sintering additives of 2 wt % Y$_2$O$_3$ (Y) and 2.5 wt% Y$_2$O$_3$+Al$_2$O$_3$ (Y + A) are added to each SiC/AlN mixture in an attempt to enhance their sinterability through liquid phase formation. It was reported that, alumina is a good additive for SiC and yttria is a good sintering aid for AlN [30,31]. Yttria and alumina can react with AlN and SiC and forms a Y-Si-Al-O-N liquid phase that can assist the densification during sintering [32]. Figs. 12 and 13 show the effect of sintering additives on the densification parameters (bulk density & apparent porosity) of SiC/AlN composites sintered at 1550° C/2 h in

solution reaction and the degree of densification and sintering such as sintering atmospheres, sintering temperature and additives are studied and discussed.

SiC composites with different AlN content (0X-4X) were sintered at 1550° C/2 h under vacuum atmosphere with a heating rate of 10° C/min without using sintering aids. The XRD patterns of the sintered composites show the presence of AlN and combination of α- and β-SiC phases as inspected in Fig. 9. AlN and α-SiC exist in the hexagonal crystal structure (2H) while β-SiC exists in a cubic crystal structure (3C). The relative intensity of AlN peaks increases gradually but slightly with increasing the AlN content in the different

Fig. 4. FESEM of β-SiC powder.

Fig. 5. TEM of β-SiC powder.

Ar/vacuuum atm without and with the addition of Y and Y + A additives.

There was a slight enhancement in the densification parameters of the samples by addition of Y and further enhancement with using Y + A due to the formation of a small amount of liquid phase during the sintering. However, the improvement was not perceptible due to the applied low sintering temperature. Higher temperatures are required in order to complete the solid solution reaction.

On the other hand, the XRD analysis of the obtained composites without and with sintering additives gave the same phases of AlN, β- and α-SiC without any appearance of yttria and alumina or any other liquid phases as investigated in Fig. 14. This case may be attributed to that; the liquid-phases may disappear before the completion of the sintering, either by incorporation into the solid phase to produce a solid solution, by crystallization of the liquid phase, or by evaporation. This type of sintering occurs in two stages, firstly transient liquid phase sintering and then solid state sintering.

In accordance, sintering temperature is increased from 1550 to 1650 and 1750/2 h under Ar/vacuum atmosphere without and with using Y and Y + A in attempts to enhance the sinterability and density of sintered SiC/AlN composites. Densification parameters of the different composites at different temperatures are clarified in Figs. 15 and 16. It was found that, with increasing sintering temperature, the densification parameters are significantly enhanced. They recorded their optimum at the sintering temperature of 1750 °C/2 h for composites without and with sintering additives. In addition, it was noticed that the apparent porosity of the different SiC/AlN composites decreases and bulk density increases gradually
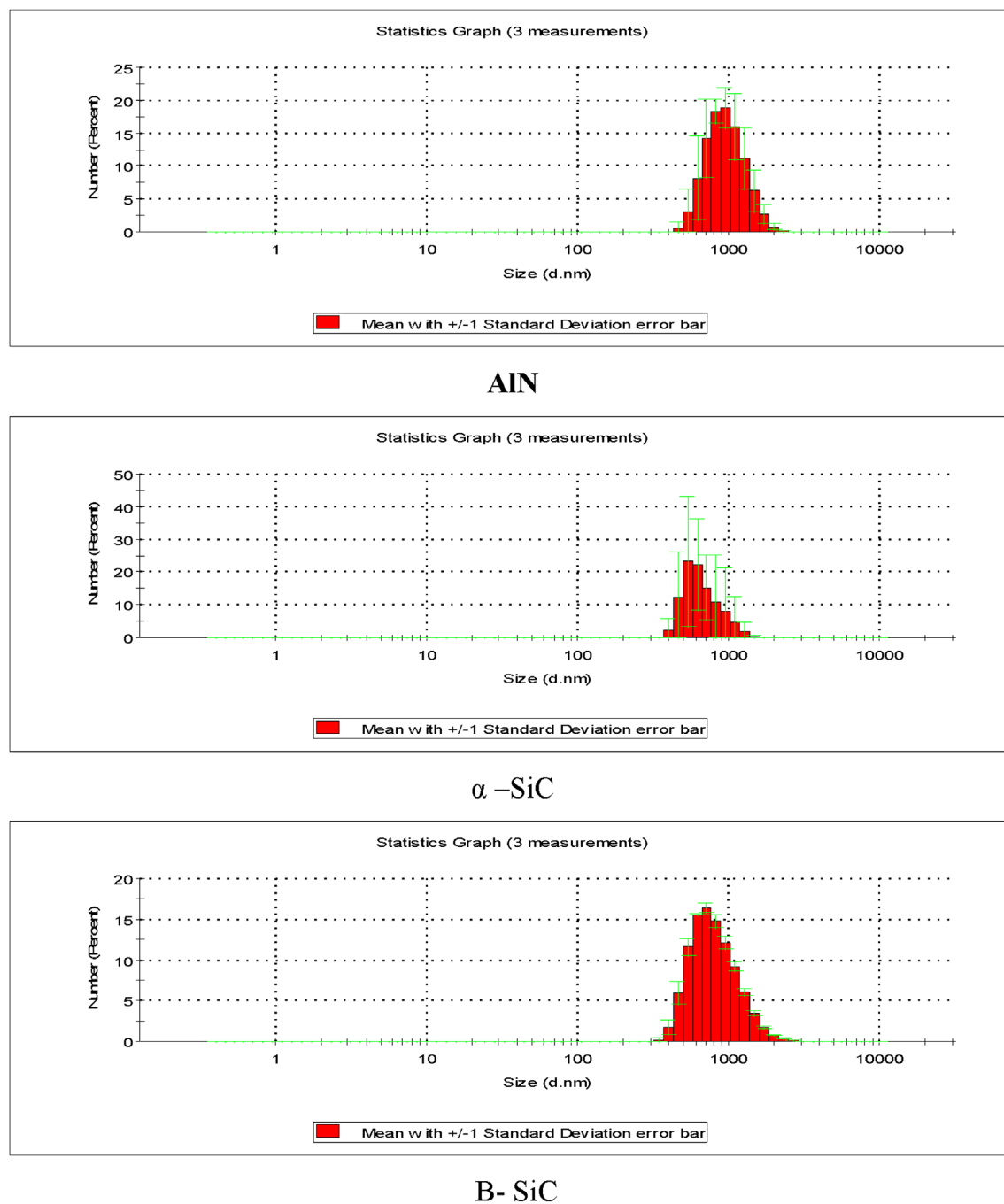
Fig. 6. FESEM of α-SiC powder.

Fig. 7. TEM of α-SiC powder.

with increasing the AlN content to reach to their maximal in composite 4 with 40% AlN. This can be explained by increasing the amount of the formed liquid phase with increasing AlN content which agreed with some other works [30–33].

Moreover, after studying and comparing the densification parameters of different SiC/AlN composites without and with the addition of ytrria and yttria + alumina at sintering temperature of 1750 °C/2 h as noticed in Figs. 17 and 18. It was deduced that SiC/AlN composites with 2.5% Yttria + alumina addition gave the highest density and lowest porosity. Therefore ytrria with alumina are found to be better sintering additives than ytrria only. Composites with Y + A addition were considered the optimal and selected for the further studies. They gave the highest density of

2.12 g/cm^3 for composite 4 YA which represents about 63.5% of theoretical density. So that, addition of Y + A to SiC/AlN ceramics promotes the sinterability and the formation of solid solutions. However, the different composites with Y + A addition are still suffering from low density and high porosity percentage. Increasing temperature higher than 1750 °C is still required to enhance the density and activate the liquid phase formation at high temperature.

Subsequently, sintering temperature is increased from 1750 to 2080 °C/2 h in the Ar/vacuum atmosphere for the different SiC/AlN composites with 2.5% Y + A. Investigation of phase analyses of different composites of such conditions is clarified in Fig. 19. It was noticed that, with increasing sintering temperature to 2080° C, All

AlN

α −SiC

B- SiC

Fig. 8. Particle size distribution of AlN, β-SiC and α SiC powders.

3c β-SiC phases have replaced with 6H α-SiC phases that confirms the β → α-SiC transformation resulting from sintering at high temperatures [34–36].

2H and 6H silicon carbides are identified as the major phases with the absence of β-SiC phase for sample 0 YA. With increasing AlN content in composites, the intensity of SiC phases decrease and AlN increases, Fig. 19. Additionally, Diffraction peaks of 2H SiC/AlN solid solutions increase with increasing AlN content and sintering temperature. This indicates the increase of solid solution reaction with the AlN addition at high temperatures compared to samples sintered at lower temperature, Figs. 9 and 14.

Moreover, it was observed that in composites 0 and 1 YA at 2θ value of ≈ 38°, only 6H phases are present. However, starting from composite 2 YA to 4 YA, this peak was shifted with 2H AlN to form 2H-6H split peaks. It is believed that this split peak is concerned to SiC/AlN solid solution as agreed with other works [29,32,37]. This explains increasing the peak intensity with increasing AlN content and confirms the presence of both 2H and 6H solid solutions of SiC/AlN composites.

Furthermore, apparent porosity, bulk and relative densities of these composites and their comparison with composites sintered at 1750 °C/2 h are illustrated in Figs. 20 and 21 respectively. It was found that, with increasing sintering temperature to 2080 °C/2 h, density of SiC rich composites is sharply increased compared to composites sintered at 1750 °C/2 h. For example, density of 0 YA composite increased from 1.89 to 2.66 g/cm^3 (80% of theoretical

Table 1
The designations of SiC/AlN composites without and with sintering additives.

Sample	SiC (wt%)	AlN (wt)	Sintering aids
0 X	100%	0%	No additives
1 X	90%	10%	
2 X	80%	20%	
3 X	70%	30%	
4 X	60%	40%	
0 Y	100%	0%	2% Yttria
1 Y	90%	10%	
2 Y	80%	20%	
3 Y	70%	30%	
4 Y	60%	40%	
0 YA	100%	0%	0.9% Yttria +1.6% Alumina
1 YA	90%	10%	
2 YA	80%	20%	
3 YA	70%	30%	
4 YA	60%	40%	
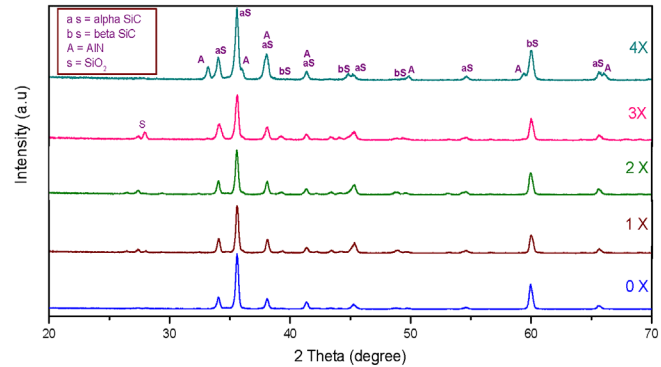
Fig. 9. XRD patterns of SiC/AlN composites (0X-4X) sintered at1550° C/2 h under vacuum.

density) when the sintering temperature increased to 2080 °C/2 h. This can be attributed to the formation of higher liquid phase amount at higher sintering temperature. In contrast, with increasing AlN content, bulk density gradually decreases and apparent porosity gradually increases of AlN rich composites. This behavior can be explained by the mass transfer by vapor condensation which is dominant in AlN rich composites. AlN vaporizes more easily than SiC, and mass transfer readily occurs by vapor condensation at high temperature [33]. In contrast to mass transfer
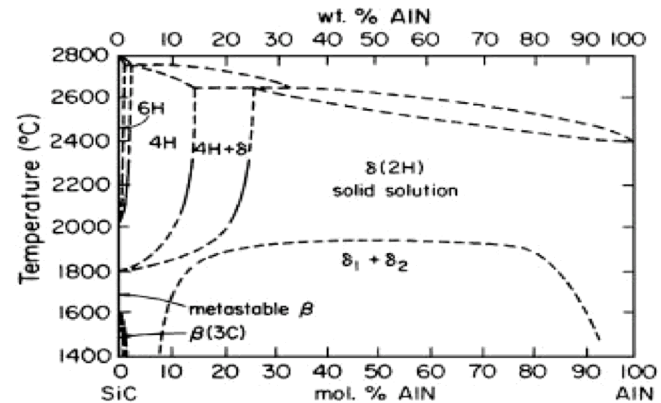
Fig. 10. Tentative phase diagram of the SiC/AlN system.
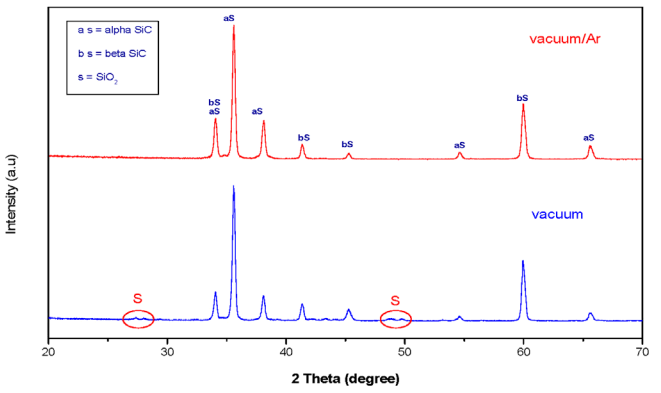
Fig. 11. XRD patterns of composites 0X sintered at1550° C/2 h under vacuum and Ar/vacuum atmospheres.

Table 2
Densification parameters of different SiC/AlN composites sintered at1550 °C/2 h

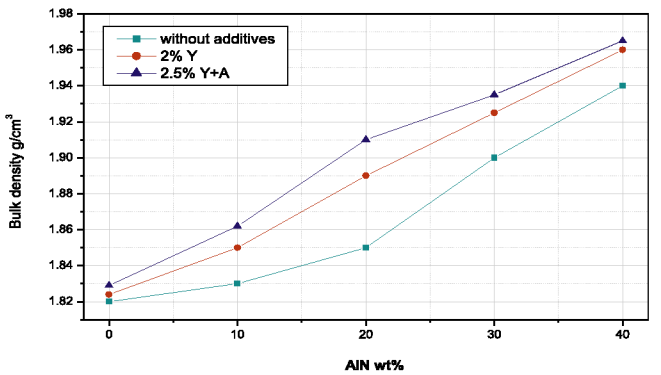| Samples	Apparent Porosity %	Bulk Density g/cm^3	Relative Density %
0 X	46.2	1.82	56.69
1 X	46.1	1.83	56.92
2 X	45.4	1.85	57.45
3 X	44.2	1.9	59.53
4 X	42.5	1.94	60.06

Fig. 12. Bulk density of SiC/AlN composites without and with sintering additives sintered at 1550 °C/2 h
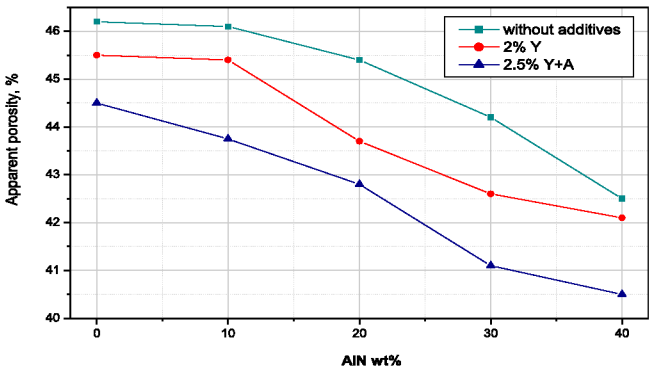

Fig. 13. Apparent porosity of SiC/AlN composites without and with sintering additives sintered at 1550 °C/2 h.
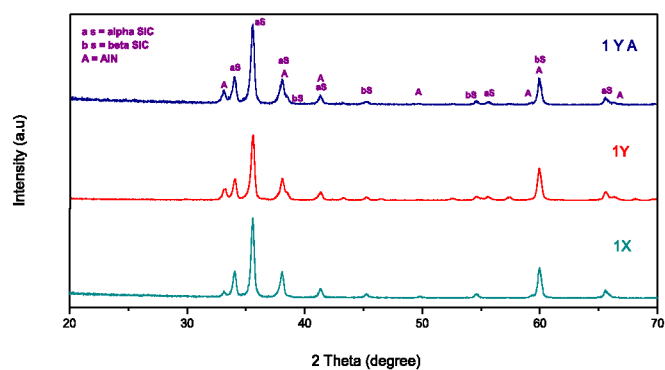
Fig. 14. XRD patterns of SiC/10 wt%AlN composite without and with sintering additives sintered at 1550 °C/2 h.
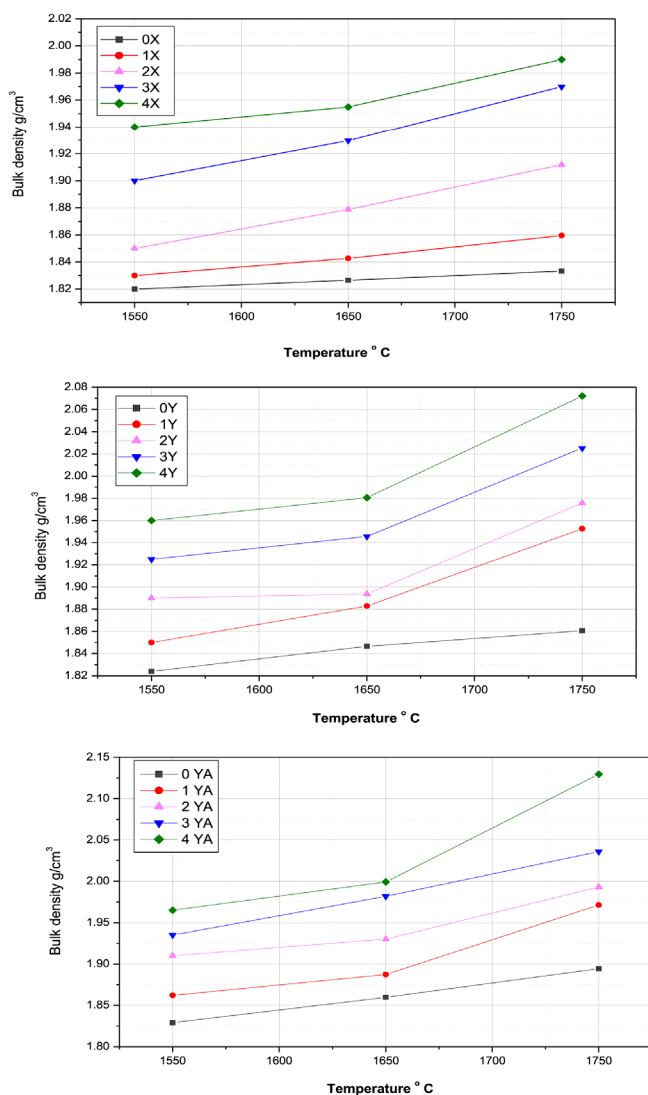

Fig. 15. Bulk density of different SiC/AlN composites without and with additives sintered at different temperature.
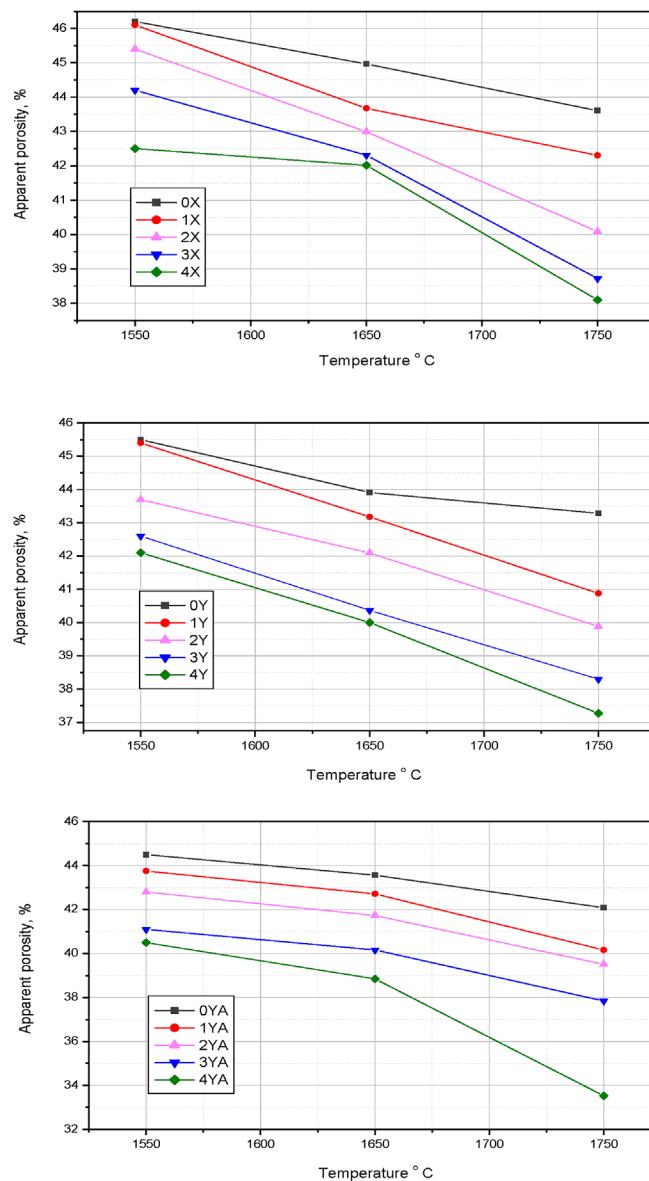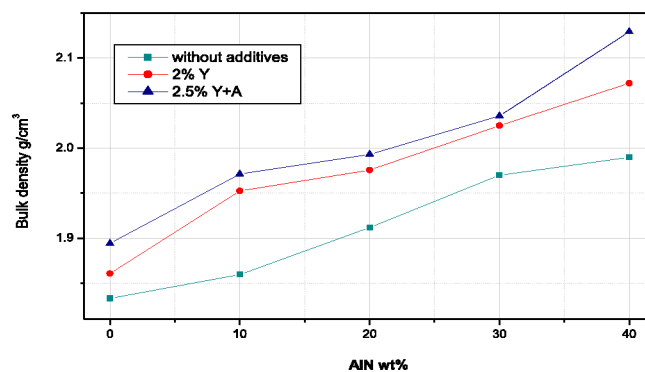

Fig. 16. Apparent porosity of different SiC/AlN composites without and with additives sintered at different temperature.

Fig. 17. Bulk density of SiC/AlN composites without and with sintering additives sintered at 1750 °C/2 h.

by grain boundary diffusion or volume diffusion, mass transfer by vapor condensation involves grain growth with no densification (ref). This can explain the reduction of the bulk density with increasing AlN content. In addition, AlN was found to be an
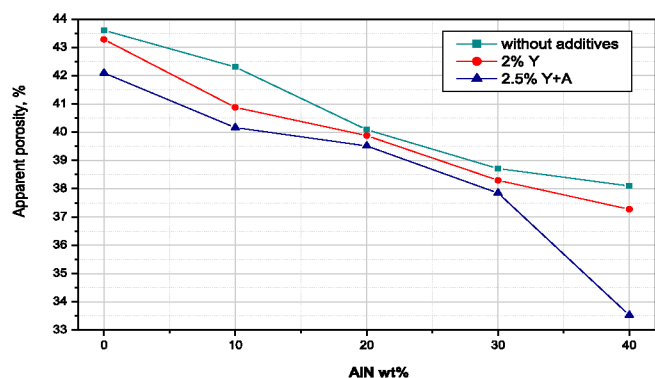
Fig. 18. Apparent porosity of SiC/AlN composites without and with sintering additives sintered at 1750 °C/2 h.

influential factor in determining the weight loss accompanied by SiC/AlN composites sintering. It was found that, weight loss of the different SiC/AlN composites increases with increasing AlN content at high sintering temperature (higher than 2000 °C) [38]. In contrast, weight loss decreases with increasing AlN content in composites sintered at 1700–1800 °C [38]. So that, sintering of different SiC/AlN composites at 2080 °C/2 h in an Argon/vacuum atmosphere with the addition of 2.5% Y + A is selected as the optimum conditions for producing controlled porosity and well sintered SiC/AlN composites.
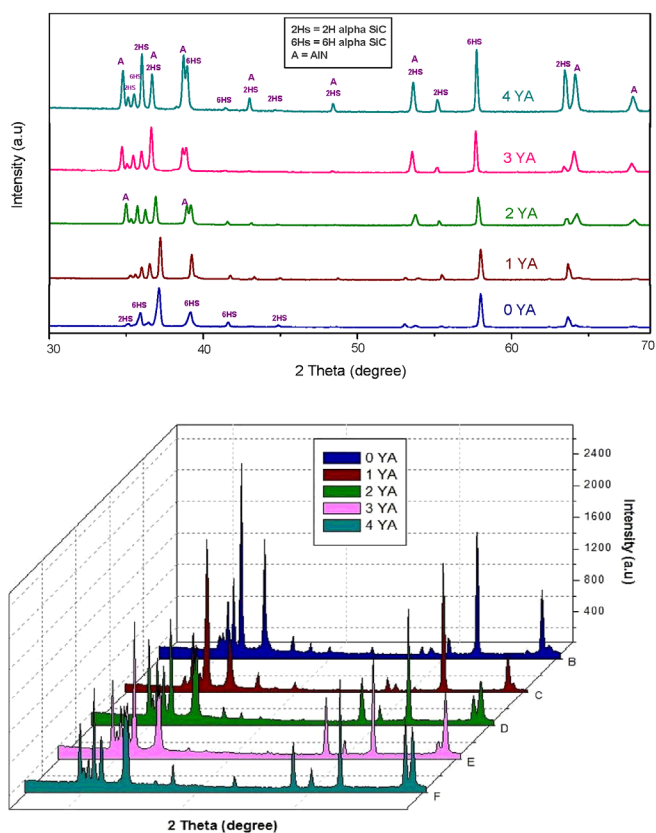

Fig. 19. XRD patterns and 3D simulation of different SiC/AlN composites (0YA-4YA) sintered at 2080° C/2 h in Ar/vacuum.
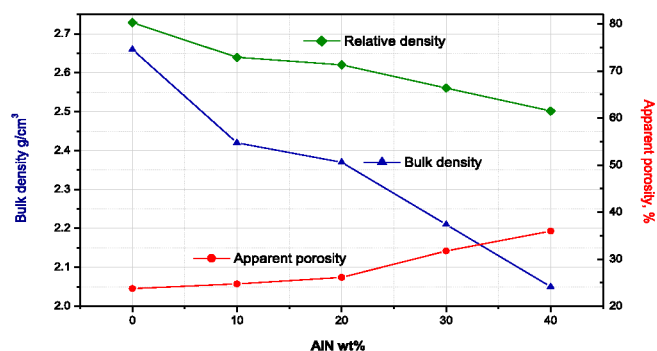

Fig. 20. Densification parameters of different SiC/AlN composites sintered at 2080 °C/ 2 h with 2.5% Y + A.

3.3. Microstructure examination

Fig. 22 shows the microstructure investigation of SiC/AlN ceramics with different compositions (0–40% AlN) sintered at 2080 °C/2 h in an Argon/vacuum atmosphere with 2.5% Y + A addition. Low magnification micrographs show uniform and gradual distribution of AlN and SiC from composite 0 (0% AlN) to composite 4 (40% AlN). The matrix for all composites shows a homogeneous distribution resulting from the good homogeneity achieved in the mixing process and from using small sized particles. However, high magnification images illustrate the detailed morphology of each composite structure. Sample 0 YA gave a relatively fine grained microstructure comprised of dark elongated grains of SiC and white spherical grains of Y + A with small content. The rod like structure behavior of SiC grains is attributed to the β to α -SiC transformation [39]. Despite the occurrence of the β - to α -SiC transformation, the microstructure did not reveal any grain growth behavior.

Furthermore, it was impressive to find that, insertion of AlN to SiC ceramic extremely affects on its microstructure. With addition of AlN, composites predominantly show elongated grain morphology. This can be attributed to the formation of a liquid phase during sintering. With increasing AlN content, the amount of liquid phase formed increases. It gave an ideal microstructure as that of liquid phase sintering in the pressureless sintered AlN. In liquid phase sintering, the sintering additive either melts or reacts with another sintering additive or the major component to form a liquid, usually eutectic. This eutectic liquid phase formation governs the effectiveness of the sintering process [39]. This favors
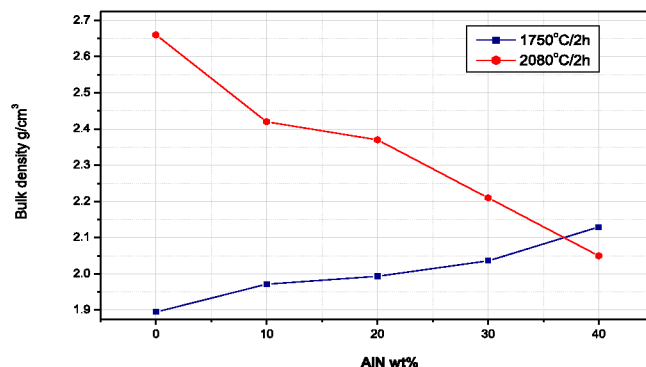

Fig. 21. Bulk densities of different SiC/AlN composites sintered at 1750 °C/2 h and 2080 °C/2 h with 2.5% Y + A.
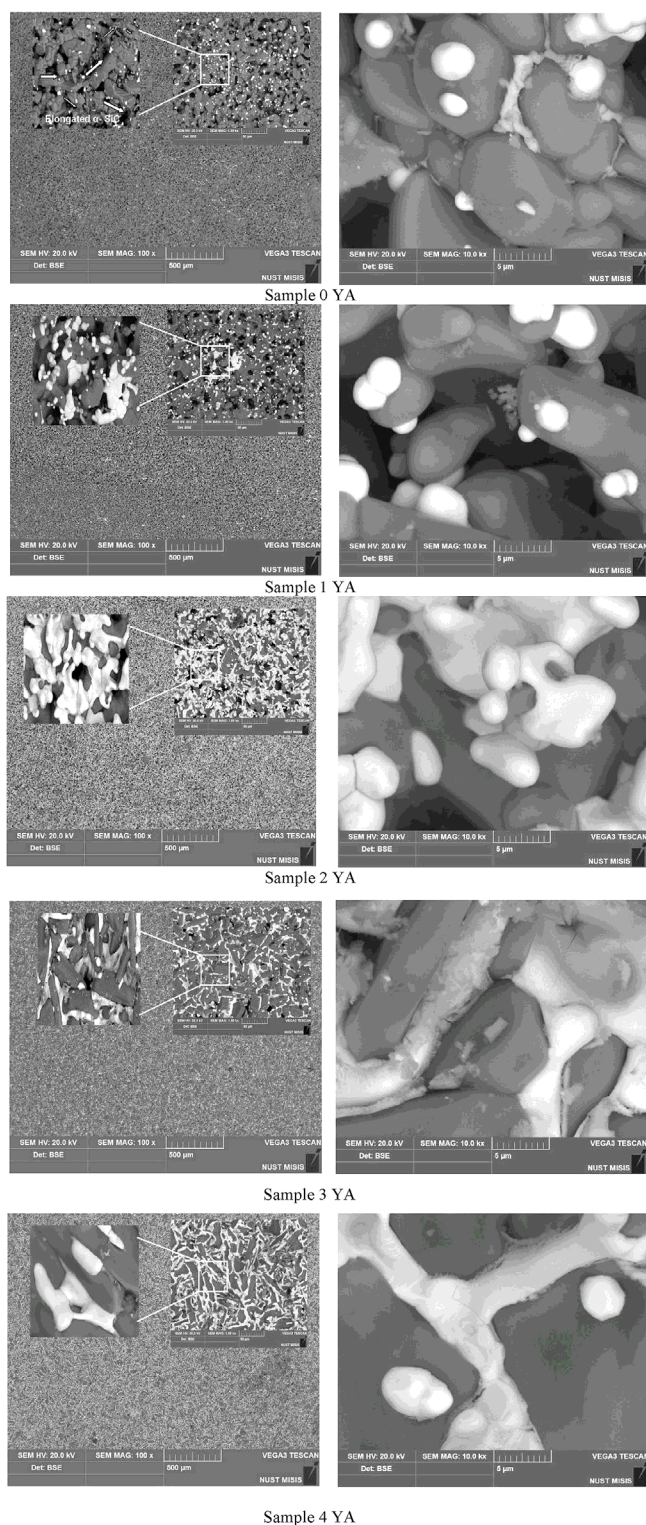
Fig. 22. Microstructure of different SiC/AlN composites sintered at 2080 °C/2 h.

inter-diffusion and formation of completely homogenous solid solutions of AlN and SiC as noticed in sample 4 (Fig. 22). The formation of this solid solution was confirmed by other works [40,41]. Culter et al. results were the first which conducted that, SiC and AlN react and form an extensive solid solution at a temperature between 1800 and 2100 °C [42].

In details, formation of SiC/AlN solid solution takes place through several steps [32,43]. Firstly, the second-phase particles, AlN, vaporize from the large powder surface, and then AlN is deposited on the surface of the SiC powders, thus decreasing in size. Subsequently, AlN on the SiC surface diffuses into the SiC grain body, and finally SiC and AlN form a SiC-AlN solid solution layer on the surface of SiC. Moreover, not only the grain growth of SiC is suppressed, but also the grains are refined by the nucleation of AlN in the solid solution reaction.

This behavior can be explained to that, the solid vaporization pressures of AlN and SiC are 14 and $1.23*10^{-3}$ mmHg at 1900 °C [33]. Of course, the vaporization and the diffusion rate of AlN solid far exceeds that of SiC at 1950–2000 C. It is imagined that the microstructure changes during the sintering process, as shown in Fig. 22.

On the other side, addition of yttria and alumina sintering additives to SiC/AlN composites was found to promote and enhance both the densification process and the formation of solid solution as discussed above. Despite the occurrence of the β-to α-SiC transformation, the microstructure gave fine grains with homogenous structure and did not reveal any grain growth behavior.

It can be summarized that, the addition of AlN to SiC lead to form a homogeneous microstructure with expected good mechanical properties and a stress free structure.

3.4. Thermal diffusivity and thermal conductivity of SiC/AlN composites

Different SiC/AlN composites sintered at 2080 °C/2 h with 2.5% Y + A addition are undergone to thermal diffusivity and conductivity measurements at temperature range 25–300 °C as observed in Figs. 23 and 24.

Thermal diffusivity considers a specific property for characterizing unsteady heat conduction of the material. Its value describes how quickly a material reacts to a change in temperature. A material with a high thermal diffusivity is a good diffuser of thermal energy while a material with a low thermal diffusivity is much slower at diffusing thermal energy. It was observed that, different SiC/AlN composites gave good thermal diffusivity and conductivity values. Sample 0 gave the highest thermal conductivity and diffusivity values. Thermal conductivity values of the composites change with weight percentage (wt. %) of AlN as represented in Fig. 24. As revealed, thermal conductivity of SiC/AlN gradually decreased in a linear manner with increasing weight percent of AlN up to 40%. A minimal value of 10.6 W/m.K was obtained for 40% AlN composite
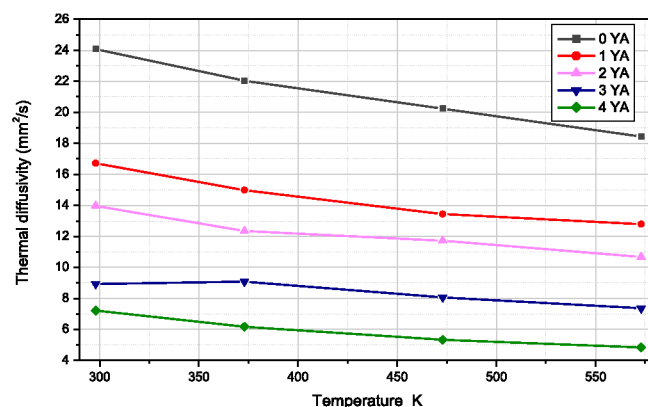

Fig. 23. Thermal diffusivity of different SiC/AlN composites sintered at 2080 °C/2 h.
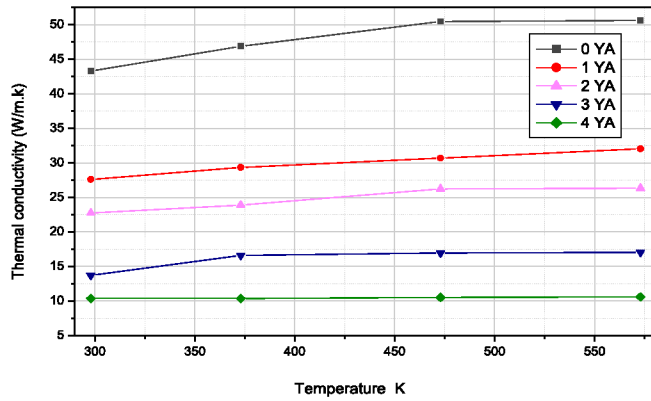
Fig. 24. Thermal conductivity of different SiC/AlN composites sintered at 2080 °C/2 h.
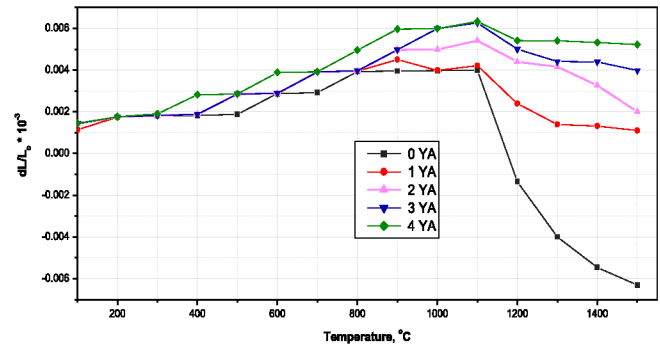

Fig. 25. Linear thermal expansion of different SiC/AlN composites as a function of temperature.

Fig. 26. CTE of different SiC/AlN composites as a function of temperature.

and a maximal value of 50.6 W/m.K was produced for 100% SiC composite. Hence, the addition of AlN to SiC caused drooping in thermal conductivity values.

The main reason is that, thermal conductivity values are significantly influenced by the addition of other phases and porosity level [44]. Since the addition of AlN and increasing its content led to reduction of density and increasing porosity as explained in the part of densification parameters. So that increasing of AlN wt% leads to deterioration of thermal conductivity values. In addition, this behavior by decreasing thermal conductivity with increasing AlN content can be explained by the formation of glassy liquid phase at the grain boundaries and increasing its amount with increasing AlN percentages [45]. Whereas, increasing AlN content lead to increasing the formation of 2H solid solution in the ceramics as explained in the microstructure and other previous works [44–48]. Bentsen has reported that, thermal conductivity of SiC/ AlN composites is lower than that of monolithic SiC or AlN due to the formation of the solid solution [44].

On the other side, it was found that, thermal conductivity values increase gradually but slightly with increasing temperature for all samples. This can be explained as, in non-metals; the heat is transferred by lattice vibrations, as atoms vibrating more energetically at one part of a solid transfer that energy to less energetic neighboring atoms in the form of propagating lattice waves, which are quantized as phonons. Hence, with increasing temperature, the phonon conduction increases and the thermal conductivity increase.

3.5. Thermal expansion and its coefficient

Linear thermal expansion and its coefficient (CTE) of the different SiC/AlN composites sintered at 2080 °C/2 h in Ar/vacuum with 2.5% Y + A as a function of temperature are shown in Figs. 25 and 26. Generally LTE and CTE of the different composites showed the same sequence and behavior. It was noticed that, linear thermal expansion and its coefficient of the different composites are linear increasing with the temperature up to 1000 °C. However, at temperature above 1100 °C, a sharp deviation and abrupt reduction were observed for the different compositions. This observed contraction instead of expansion with increasing temperature is a sign of sintering and densification process, Fig. 25. The more interesting is the negative thermal expansion behavior of 100% SiC (0 YA) composite; its linear shrinkage started at a temperature above 1100 °C and further heating has decreased its elongation rapidly to zero and finally to negative behavior or contraction at temperatures above 1200 °C. This negative thermal expansion behavior of SiC did not report before in other previous works. It was
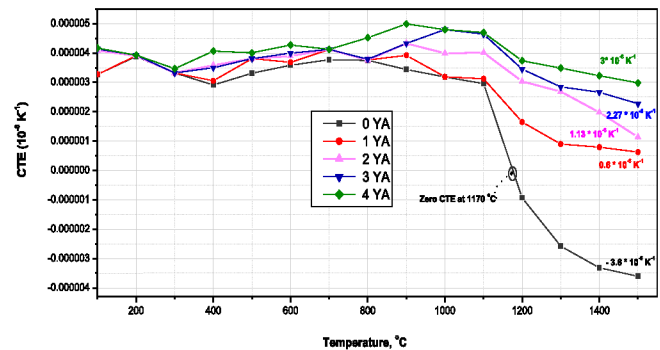
strongly agree with the densification behavior of this composite in which it has the highest densification level compared to the other composites as discussed before. Otherwise, with increasing AlN content from composite 1 YA to 4 YA, the thermal expansion showed the same behavior as 0 YA, but are gradually increased due to the higher thermal expansion of AlN. On the other side, CTE of the different SiC/AlN composites followed the same LT demeanor as illustrated in Fig. 26. CTE values of different composites recorded a gradual increase with the increase of AlN content. This increment in CTE values with increasing AlN content can be realized from the higher CTE of AlN ($\approx 4.5 *10^{-6} K^{-1}$) when compared to SiC ($\approx 4 *10^{-6} K^{-1}$) [36]. Specifically, at temperature above 1100 °C, CTE values are abruptly decrease with increasing temperature up to 1500 °C. 0 YA composite gave the lowest CTE values with negative thermal expansion coefficient at high temperature. For example, at a temperature of 1500 °C, CTE recorded its minimal at 0 YA composite with a negative value of $-3.6 * 10^{-6} K^{-1}$ and its maximal in composite 4 YA with value of $3* 10^{-6} K^{-1}$. The characteristics of the formed liquid phase and the residual stress resulted from the phase transformation of SiC could explain the observed low and negative thermal expansion coefficient of the different SiC/AlN ceramics.

Moreover, it was indicated that, when a polycrystalline sample is subjected to a temperature change, it is prone to microcracking or grain boundary separation even in the absence of porosity. These processes and the internal crack closure during heating and crack open during cooling, caused by the temperature gradients inside the sample, may lead to hysteresis and to an apparently negative CTE, even if the true CTE is positive [49–52].

The low and negative thermal expansion coefficient value of different SiC/AlN composites at high temperatures can be attractively and strongly nominated them in many interesting high temperature, engineering, electronic and structural applications.

4. Conclusions

SiC/AlN composites with high density and high thermal properties have produced by pressureless sintering of SiC and AlN at the sintering temperature of 2080 °C in Ar/vacuum with 2.5% Y + A addition. Influence of different parameters on sintering and densification of the different composites such as sintering atmosphere, additives and temperature was inspected. It was found that increasing sintering temperature by using alumina and yttria additives has promoted the sintering process and densification behavior through liquid phase formation. Increment of AlN % led to increasing the solid solution reaction, but decreasing the densification parameters in the different composites at high sintering temperatures. XRD analysis and microstructure examination confirm the β → α SiC transformation through the appearance of 4H SiC with elongated grain morphology. Insertion of AlN to SiC leads to form fine grain homogenous microstructure without any noticeable grain growth behavior. Thermal conductivity and diffusivity values were significantly relying on the densification behavior and AlN content. Coefficient of thermal expansion of different SiC/AlN composites was mainly dependent on temperature and AlN%. Nevertheless, it attractively recorded low and negative values at high temperatures. The present study proposes that different properties of SiC/AlN system are controllable if adding low AlN content. Evaluations of different SiC/AlN ceramics characteristics have nominated them to be used in solar energy and high temperature applications.

References

[1] T. Fend, High porosity materials as volumetric receivers for solar energetics, Opt. Appl. XL (2) (2010) 272–283.
[2] H. Fricker, Studie über die Möglichkeiten eines Alpenkraftwerkes, Bull. SEV/VSE 76 (1985) 10–16 (in German).
[3] C.J. Winter, R.L. Sizmann, L.L. Vant-Hull, in: Solar Power Plants, Springer-Verlag, Berlin, 1991.
[4] A. Kribus, H. Ries, W. Spirkl, Inherent limitations of volumetric solar receivers, J. Sol. Energy Eng. 5 (1996) 118–151.
[5] R. Pitz-Paal, B. Hoffschmidt, M. Böhmer, M. Becker, Experimental and numerical evaluation of the performance and flow stability of different types of open volumetric absorbers under non-homogeneous irradiation, Sol. Energy 50 (1997) 60–135.
[6] T. Fend, Pitz-Paal, O. Reutter, J. Bauer, B. Hoffschmidt, Two novel high porosity materials as volumetric receiver for concentrated solar radiation, Sol. Energy Mat.&Sol.Cells 84 (2004) 291–304.
[7] M. Becker, T. Fend, T.B. Hoffschmid, R. Pitz-Paal, O. Reutter, V. Stamatov, M. Steven, D. Trimis, Theoretical and numerical investigation of flow stability in porous materials applied as volumetric solar receivers, Sol. Energy 80 (10) (2006) 1241–1248.
[8] O. Reutter, J. Sauerhering, E. Smirnova, T. Fend, S. Angel, R. Pitz-Paal, Experimental investigation of heat transfer and pressure drop in porous metal foams, in: Proceedings of ASME ICNMM2006, 4th International Conference on Nanochannels, Microchannels and Minichannels, Limerick, Ireland, 2006 paper no. ICNMM 2006–96135. June 19–21.
[9] D.L. Jiang, "Preparation and properties of SiC-AlN- Y2O3 multiphase ceramics, J. Inorg. Mater. 10 (2) (1995). China.
[10] Sheppard and Laurel M, Aluminium nitride: a versatile but challenging material, Am. Ceram. Soc. Bull. 69 (1990) 1801.
[11] G.W. Prochaska, G.R. Miller, Aluminium nitride: a review of the knowledge base for physical property development, Mater. Res. Soc. Symp. Proc. 167 (1990) 215.
[12] K.X. Chen, C.C. Ge, J.T. Li, W.B. Cao, Microstructure and thermo-kinetics analysis of CS AlN, J. Mater. Res. 14 (1999) 1944.
[13] J.-L. Huang, J.-M. Jih, Investigation of SiC–AlN system: Part II. Mechanical properties, J. Am. Ceram. Soc. 79 (5) (1996) 1262–1264.
[14] Y.-B. Pan, J.-H. Qiu, M. Kawagoe, M. Morita, S.-H. Tan, D.-L. Jiang, SiC-aln particulate composites, J. Eur. Ceram. Soc. 9 (1999) 1789.
[15] I.B. Culter, P.D. Miller, W. Rafaniello, "New materials in the Si-C-Al-O-N and related systems, Nature (London) 275 (1978) 434.
[16] I. Teusel, C. Rossel, Pressureless sintering of aluminium nitride/silicon carbide ceramics, J. Mater. Sci. Lett. 1 (1) (1992) 205.
[17] J.-L. Huang, J.-M. Jih, Investigation of SiC-AlN system: part I. Microstructure and solid solution, J. Mater. Res. 10 (1995) 651.
[18] W. Rafaniello, M.R. Plichta, A.V. Virkar, Investigation of phase stability in the system SiC–AlN, J. Am. Ceram. Soc. 66 (4) (1983) 272.
[19] J.F. Li, R. Watanabe, Preparation and mechanical properties of SiC-AlN ceramic alloy, J. Mater. Sci. 26 (1991) 4813.
[20] W. Rafaniello, K. Cho, A.V. Virkar, Fabrication and characteristics of SiC–AlN alloys, J. Mater. Sci. 16 (1981) 3479.
[21] A. Zangvil, R. Ruh, Phase relationships in the silicon carbide-aluminum nitride system, J. Am. Ceram. Soc. 71 (1988) 884.
[22] I. Jenkins, K.G. Irvine, M.G. Spencer, V. Dmitirev, N. Chen, Growth of solid solutions of aluminum nitride and silicon carbide by metal organic chemical vapor deposition, J. Cryst. Growth 128 (1993) 375.
[23] R.S. Kern, L.B. Rowland, S. Tanaka, R.F. Davis, Solid solutions of AlN and SiC grown by plasma-assisted, gas-source molecular beam epitaxy, J. Mater. Res. 8 (1993) 1477.
[24] H. Xue, Z.A. Munir, Synthesis of AlN-SiC composites and solid solutions by field-activated self-propagating combustion, J. Eur. Ceram. Soc. 17 (1997) 1787.
[25] E.M. Carrillo-Heian, H. Xue, M. Chyanagi, Z.A. Munir, Reactive synthesis and phase stability investigations in the aluminum nitride–silicon carbide system, J. Am. Ceram. Soc. 5 (2000) 1103.
[26] K.W. Chew, A. Sellinger, R.M. Laine, Processing aluminum nitride–silicon carbide composites via polymer infiltration and pyrolysis of poly-methylsilane, a precursor to stoichiometric silicon carbide, J. Am. Ceram. Soc. 82 (4) (1999) 857–866.
[27] C. Kexin, J. Haibo, Z. Heping, J.M.F. Ferreira, Combstion synthesis of AlN-SiC solid solution particles, J. Eur. Ceram. Soc. 20 (2000) 2601–2606.
[28] X. Hanning, Y. Jixiang, G. Jimimg, Y. Qiaoqin, Preparation of SiC-AlN composite powders by inorganic sol-gel processing, Trans. Nonferrous Metals Soc. China 8 (2) (1998) 301–303.
[29] R. Kobayashi, J. Tatami, T. Wakihara, T. Meguro, K. Komeya, Temperature dependence of the electrical properties and Seebeck coefficient of AlN–SiC ceramics, J. Am. Ceram. Soc. 89 (4) (2006) 1295–1299.
[30] W. Bocker, H. Hausner, Powder Metall. Int. 11 (1979).
[31] K. Komeya, J. Am. Ceram. Soc. Bull. 63 (1984) 1158.
[32] J. Wei W-C, R.-R. Lee, Pressureless sintering of AlN-SiC composites 26 (1991) 2930–2936.
[33] T.B. Camcohob, Handbook of High Melting Point Compound, China Industry publisher, China, 1965.
[34] A.H. Heuer, G.A. Fryburg, L.U. Ogbuji, T.E. Mitchell, S. Shinozaki, β → α transformation in polycrystalline SiC: I. Microstructural aspects, J. Am. Ceram. Soc. 61 (1978) 406.
[35] L.U. Ogbuji, T.E. Mitchell, A.H. Heuer, β → α transformation in polycrystalline SiC: III. The thickening of _ plates, J. Am. Ceram. Soc. 64 (2) (1981) 91.
[36] A. Malinge, A. Coupé, Y. Le Petitcorps, R. Pailler, Pressureless sintering of beta silicon carbide nanoparticles, J. Eur. Ceram. Soc. 32 (16) (2012) 4393.
[37] J.F. Li, R. Watanabe, Pressureless sintering and high temperature strength of AlN-SiC ceramics, J. Ceram. Soc. Jpn. Int. Ed. 102 (1994) 724.
[38] S. Mandal, K. Dhargupta, S. Ghatak, Gas pressure sintering of SiC–AlN composites in nitrogen atmosphere, J. Ceram. Inter. 28 (2002) 145.
[39] K. Suzuki, M. Sasaki, Microstructure and mechanical properties of Liquid_Phase_Sintered SiC with AlN and Y2O3 additions, Ceram. Int. 31 (5) (2005) 749–755.
[40] S. Ribeiro, S.P. Taguchi, F.V. Motta, R.M. Balestra, The wettability of SiC ceramics by molten e2O3(ss)/AlN E2O3 (ss) = solid solution of rare earth oxides, Ceram. Int. 33 (2007) 527.
[41] I.L. Tangen, Y. Yu, T. Grande, T. Mokkelbost, R. Høier, M.A. Einarsrud, Preparation and characterization of aluminum nitride–silicon carbide composites, Ceram. Int. 6 (2004) 931.
[42] Culter B. and Miller P.D., US Patent 4141740, 1979.
[43] Y.B. Pan, J.H. Qiu, M. Morita, S.H. Tan, D. Jiang, The mechanical properties and microstructure of SiC–AlN particulate composite, J. Mater. Sci. 33 (1998) 1233–1237.
[44] L.D. Bentsen, D.P.H. Hasselman, Effect of hot-pressing temperature on the thermal diffusivity/conductivity of SiC/AlN composites, Commun. Am. Soc. (1981) 40–41.
[45] M. Landon, F. Thevenot, Thermal conductivity of SiC–AlN ceramic materials, J. Eur. Ceram. Soc. 8 (5) (1991) 271–277.
[46] C. Zhang, X. Yao, Y. Li, H. Liang, J. Chen, J. Zhang, J. Yang, X. Li, T. Qiu, Z. Chen, X. Liu, Z. Huang, Effect of AlN addition on the thermal conductivity of pressureless sintered SiC ceramics, Ceram. Int. 41 (2015) 9107–9114.
[47] D.H.A. Besisa, E.M.M. Ewais, Y.M.Z. Ahmed, F.I. Elhosiny, T. Fend, D.V. Kuznetsov, Thermal shock resistance of pressureless sintered SiC/AlN ceramic composites, Mater. Res. Express 5 (2018) 015506.
[48] D.H.A. Besisa, E.M.M. Ewais, E.A.M. Shalaby, A. Usenko, Thermoelectric properties and thermal stress simulation of pressureless sintered SiC/AlN ceramic composites at high temperatures, Sol. Energy Mater. Sol. Cell. 182 (2018) 302–313.
[49] J.A. Kuszyk, R.C. Bradt, J. Am. Ceram. Soc. 56 (1973) 420.
[50] W.R. Buessem, N.R. Thielke, R.V. Sarakauskas, Ceram. Age 60 (1952) 38.
[51] E.A. Bush, F.A. Hummel, J. Am. Ceram. Soc. 42 (1959) 388.
[52] W.R. Buessem, Internal Ruptures and Recombinations in Anisotropic Ceramic Matfrials, Mechanical Properties of Engineering Ceramics, Interscience, New York, 1981, p. 127.