ELSEVIER

Ceramics International 27 (2001) 473–479

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Gas pressure sintering of β SiC–γ-AlON composite in nitrogen/argon environment

S. Mandal, A.S. Sanyal, K.K. Dhargupta, S. Ghatak *

Central Glass and Ceramic Research Insititute, Calcutta 700 032, India

Received 19 July 2000; received in revised form 4 August 2000; accepted 14 October 2000

Abstract

A SiC and γ AlON system was studied using β-SiC powder and a preformed spinel between Al_2O_3 and AlN corresponding to γ-AlON. A wide range of composition from 10 to 90 wt.% γ-AlON with β-SiC was studied. The composite was sintered to near pore-free dense sintered product for a wide range of composition ranging from 10 to 55 wt.% of γ-AlON content in both a N_2 and an Ar atmosphere under a gas pressure of 6 bar. The effect of sintering atmosphere on the sintered properties such as weight loss, percentage linear shrinkage, percentage apparent porosity, and bulk density of the fired samples were determined. Weight loss of the specimen was 4.3–5.5 wt.% in a nitrogen and 6.2–10.75 wt.% in an Ar atmosphere indicating substantial supression of dissociation reaction during sintering in nitrogen atmosphere. Microhardness of the sintered specimen measured by indentation under a load of 1 N was 16.5–29.81 GPa. Phase analysis by XRD studies and the other properties indicated solid solution formation between SiC and γ-AlON.

1. Introduction

Silicon carbide, well accepted as a structural material for its superior thermo–mechanical properties, is difficult to sinter for its low ionicity. Pioneering work by Prochazka [1] on pressureless sintering of silicon carbide opened up a new horizon with wide commercial possibilities. However, this method have several limitations in precision controlling of process parameters as well as requirement of very high sintering temperature, ranging 2000–2200°C. Although silicon carbide was hot pressed [2,3] to a desired density, the method was lacking in fabrication flexibility. Several studies have also been reported on the sintering of silicon carbide using liquid phase forming additives like YAG [4–7] and rare earth oxides in combination with alumina [8–13]. Alloying of SiC for either ease of processing or improvements in properties or both has often been done with Al_2OC, AlN [2,3] or in combination of both, as these and 2H form of SiC are isostructural [3,14]. Sintering in this system was also believed to be governed by the transient liquid formation [15].

The prospect of aluminium oxynitride as an alloying agent for SiC was reported two decades back [14]. Virkar et al. proposed SiC–AlON as compatible phases [15]. According to the pseudo-binary phase diagram [16], γ-AlON, a solid solution of the composition corresponding to the mole fraction of Al_2O_3: AlN = 64.3: 35.7, is of a high melting phase. γ-AlON has inverse spinel structure. If the charge neutrality is to be maintained in the structure, the following formula for the constant anion model [17] results:

$$Al_{(64+X)/3}\ \alpha_{(8-X)/3}\ O_{(32-X)}\ N_X$$

where, α is a cation vacancy (−), or an interstitial (+). Corbin [16] reported that cation vacancy lay in the octahedra and decrease with increase in AlN content. According to the Ellingham diagram drawn with the data set of Willems et al. [18], AlON is stabilised by entropy. Now entropy is a measure of disorder and is related by the equation: $\Delta S = R\text{-ln}\ (W)$, where, W is the number of possible configuration. Therefore, the increase in the cationic vacancy in the octrahedral site up to a certain extent should lead to an increase in the number of possible configurations of the cationic vacancy. Thus, there is a tendency of γ-AlON to change in a more cation deficient oxynitride composition, wherein the number of possible configurations would be maximum and hence the entropy, to ensure its thermodynamic stability. To enjoy this stability, some cationic transfer should have occurred. It leads to the densification of γ-AlON by volume

* Corresponding author.

0272-8842/01/$ - see front matter
PII: S0272-8842(00)00106-1

diffusion. It is purely theoretical speculation on the basis of the report of Corbin [16], McCauley [17] and Willems et al. [18] and confirmed by Ado et al. [19], who reported that, γ-ALON densifies by volume diffusion mechanism. Richards et al. [20] suggested ionic conductivity leading to bulk ionic diffusion as the possible mechanism. On the contrary, Maguire et al. [21] explained the transparency developed in sintered γ-AlON by assuming transient liquid phase formation during early stages of densification. Considering all the above properties it may be assumed that, γ-AlON is a reactive material with different possible modes of molecular and ionic movements, which can be utilised for preparing the SiC-γ-AlON composites due to their structural similarities.

From the fact of similarity in crystal structure of γ-AlON with β-SiC and high reactivity of γ-AlON as discussed above, it is posiible to prepare β-SiC-γ-AlON composites on which not much work is reported in the literature [15,22]. In the present investigation the densification of β-SiC and γ-AlON composite was studied mainly for the preparation of a dense compact with a possible interpretation of the processes involved.

2. Experimental[1]

β-SiC powder (Superior Graphite, USA, surface area: 15 m^2/g), alumina powder (Cerac, USA) and AlN powder (H. C. Starck, Germany) were selected for the study of the β-SiC-γ-AlON composite.

2.1. Preparation of the additive

Alumina and AlN powder in the mol ratio of 64.3:35.7 were intimately mixed by attrition milling using acetone as a liquid medium. The milled powder was dried and sieved through 100 mesh B.S. The dried powder was then fired at 1850°C in nitrogen atmosphere for 2 h.

2.2. Preparation of green compacts and sintering

β-SiC powder and 10–90 wt.% of additive as prepared in 2.1 were mixed thoroughly in acetone medium in an attritor using alumina balls. The attrited powder was wet-sieved, dried and pressed isostatically to form pellets of 20 mm. diameter under a pressure of 250 MPa. The pressed pellets were sintered at 1950°C in a graphite resistance furnace (Astro, 1000-3560-F8204025, USA). The temperature of the furnace was sensed by graphite/boron-graphite themocouple. The accuracy of the measurement was ± 5°C. The samples were put into a graphite crucible using a packing material having the same composition to that of the specimens to be sintered. A high purity N_2/Ar gas atmosphere was maintained during sintering. The gas pressure was maintained at 6 bar at the final sintering temperature.

The sintering profile followed the schedule: room temperature to 1000°C, 15°C/min, 1000^0C to sintering temperature, 20°C/min, hold at the sintering temperature for 1 h, followed by natural cooling by continued water circulating cooling system of the furnace.

2.3. Measurement of properties

The weight loss and shrinkage were measured for the sintered samples. Apparent porosity and bulk density were determined by Archemedes' principle by a water displacement method. The pellets were cut cross-sectionally by a slow speed cutting machine for X-ray diffraction studies on the interior surface after ultrasonic cleaning in acetone medium, using CuK_α target and Ni filter under 40 kV, 20 mA. Hardness values were determined by using a load of 1 N in a microhardness tester fitted with a Vicker's square pyramidal indenter.

3. Results

The X-ray diffraction patterns (Fig. 1) of the prepared additive (described in Section 2.1) indicated the formation of γ-AlON. The specific gravity of the powder was found to be 3.69 g/cc, which also supported the formation of the desired phase.

3.1. Weight loss and linear shrinkage

When composition in the range of 10–55 wt.% of γ-AlON was sintered in N_2 atmosphere, weight loss was found to be almost independent (S.D. = 0.2581) of the composition used (Fig. 2). But when Ar was used during sintering, the weight loss was found to increase slowly with γ-AlON content up to 40 wt.% beyond which it increased rather steeply. Beyond 55 wt.% of γ-AlON content, the dissociation of the specimens was very high in both N_2 and Ar atmosphere and except XRD analysis, the other properties could not be studied as the specimens were severly disintegrated.

Linear shrinkage increased progressively with increasing γ-AlON content for both the systems fired in N_2 as well as in Ar atmosphere (Fig. 2). Again, the increment in linear shrinkage with γ-AlON content was found to be steeper when the sample was fired in N_2 atmosphere than that fired in Ar atmosphere.

3.2. Apparent porosity, bulk density and true density

For the sintered specimens fired in N_2 as well as in Ar atmosphere apparent porosity indicating open pore, was found to decrease from 3% (at 10 wt.% γ-AlON) to nearly zero percent at γ-AlON content of 35–40 wt.%,

[1] Preparation part is protected in India.

then increased again to a value of 1.5–2% (at 55 wt.% γ-AlON content) (Fig. 3).

Theoretical density was calculated by assuming the presence of only two phases β-SiC and γ-AlON in the sintered sample. It was done with some approximation as there was some evidence of the formation of solid solution of β-SiC and γ-AlON during sintering which will be discussed in Section 3.3. It was found from Fig. 4 that %T.D. was greater for the sample fired in N_2 atmosphere than that fired in Ar atmosphere. When the specimens were sintered in N_2, %T.D. was found to increase with γ-AlON content reaching a maxima at about 45 wt.% followed by a slow decrease. But, when the sample was fired in Ar atmosphere the %T.D. tended to increase for 10–25 wt.% γ-AlON content, remained more or less constant up to 50 wt.% of additive content and above that it decreased steeply.

3.3. XRD analysis

XRD-analysis revealed the existence of cubic solid solution (C_{SS}), as the *d*-value of relative intensity 100 for pure 3C (0.2520 nm) was shifted with increasing γ-AlON content, when the sample was fired in N_2 as well as in Ar atmosphere. It was evident from Fig. 5 that, the peak for cubic solid solution emerged as the major peak along with γ-AlON, when the sample containing 40 wt.% γ-AlON was fired in N_2 atmosphere. The peak for $2H_{SS}$ was also observed, but to a small extent. But, when the γ-AlON content was 70 wt.% AlN was emerged as one of the major phases (Fig. 5).

The peak for $2H_{SS}$ was found as one of the major phases along with C_{SS} and γ-AlON (Fig. 5) for the sample containing 40 wt.% γ-AlON fired in Ar atmosphere.

Lattice parameter was determined for SiC- γ-AlON composites sintered at 1950°C in N_2 atmosphere. Compositions selected were 10, 25, 35, 40, 45, 50 and 55 wt.% γ-AlON respectively. Results are shown in Fig. 6. Lattice parameter of pure β-SiC is shown as reference. Lattice parameter was found to decrease up to 45 wt.% γ-AlON followed by a steep rise.

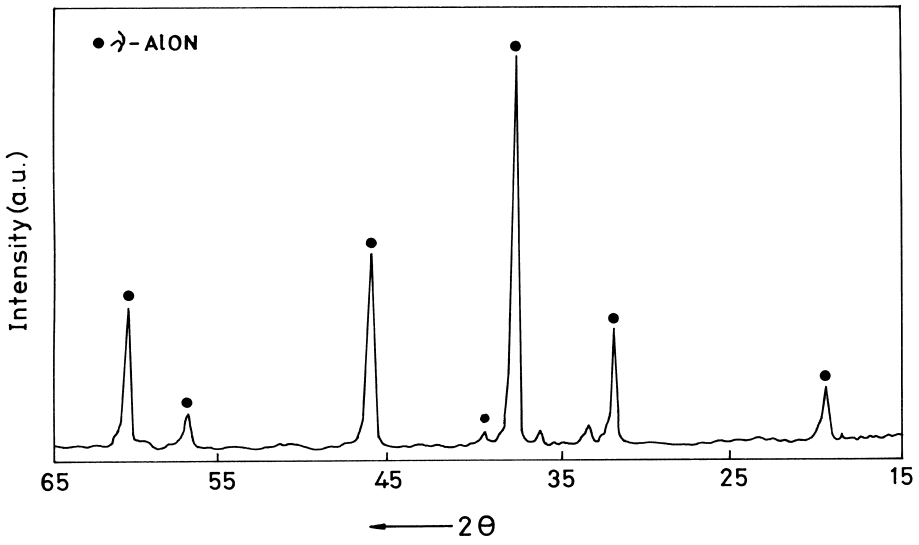

Fig. 1. XRD patterns of the γ-AlON powder.

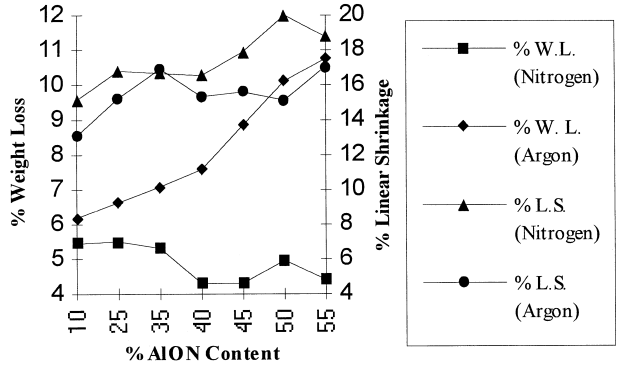

Fig. 2. Plot of % weight loss and % linear shrinkage vs. γ-AlON content (wt.%).

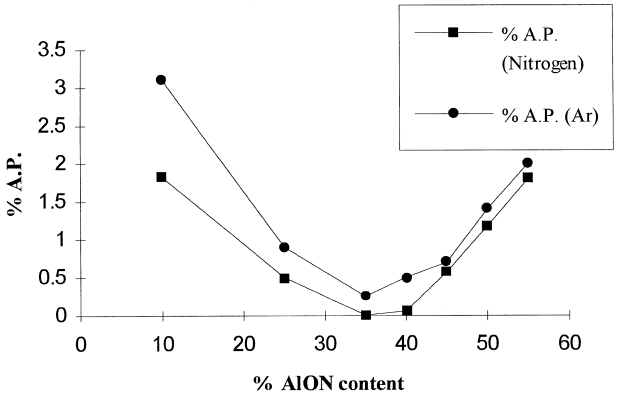

Fig. 3. Plot of % A.P. vs. γ-AlON content (wt.%).

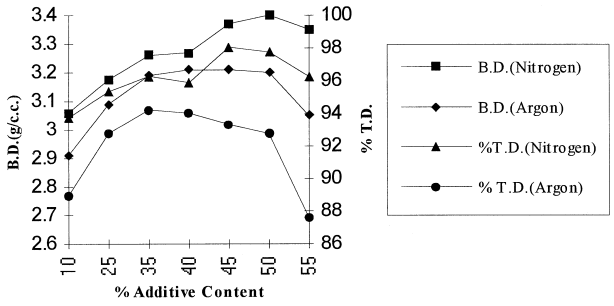

Fig. 4. Plot of B.D. (g/cc) and %T.D. vs. γ-AlON content (wt.%).

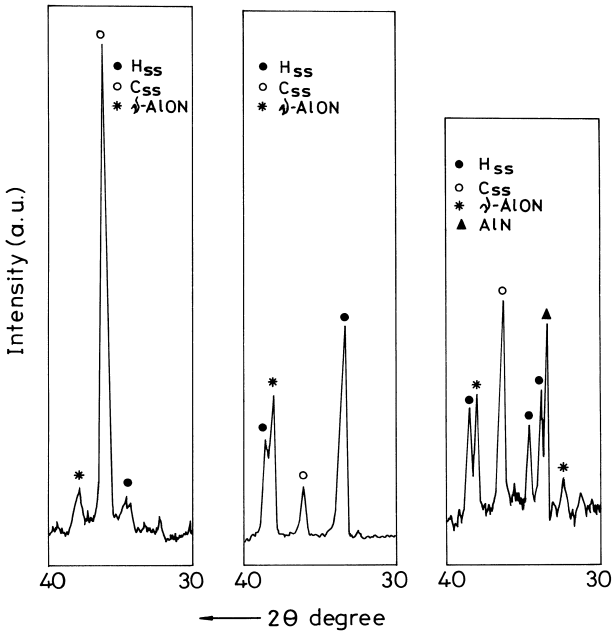

Fig. 5. XRD patterns of the sintered samples having 60 wt.% SiC + 40 wt.% γ-AlON in N_2 atmosphere (left), Ar atmosphere (middle) and 30 wt.% SiC + 70 wt.% γ-AlON fired in N_2 atmosphere (right).

3.4. Hardness

A load of 1 N was chosen for the hardness measurement, since it optimized the indentation size which would still be encompassed by a particular phase. Hardness value increased with increasing γ-AlON content up to 40 wt.%. Beyond this the hardness decreased slowly when the sample was fired in N_2 atmosphere. The same trend was observed for the sample fired in Ar atmosphere, but the maximum value of hardness was noted at 50 wt.% γ-AlON content and hardness decreased afterwards (Fig. 7).

4. Discussion

In the analysis of the above results it was noted that though sintered sample with almost theoretical density was obtained when sintered in both nitrogen and argon atmosphere, the chemical processes involved were different.

Comparative account of different sintering characteristics of the two systems is summarized below.

Weight loss of the sample sintered in nitrogen atmosphere was always smaller (4–5.5%, S.D. = 0.2581) than that sintered in argon atmosphere (6–10%). Weight loss of the sample sintered in nitrogen atmosphere was almost independent of the amount of γ-AlON used in the composites. In contrast, weight loss of the sample sintered in argon atmosphere increased slowly up to 40 wt.% γ-AlON content and above that it increased sharply. In the both nitrogen as well as argon atmosphere, the sample was disintegrated when γ-AlON content was 60 wt.% or more.

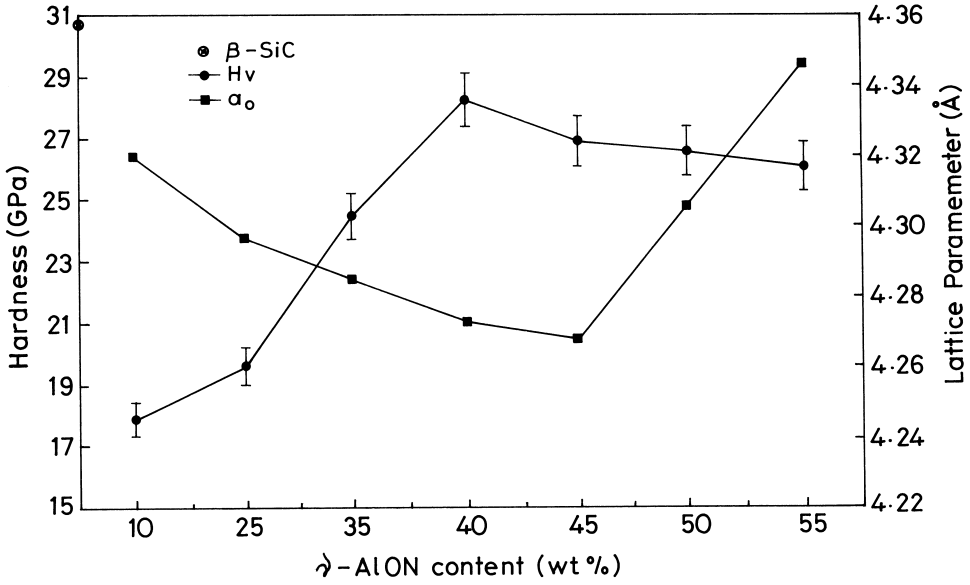

Fig. 6. Plot of change in lattice parameter and microhardness of the sample sintered in N_2 atmosphere with wt.% of γ-AlON content.

Weight loss of specimen is explained by considering various reaction as shown below with reference to the phase analysis of the sintered material.

SiO_2 present as an aerial oxidation product of SiC would contribute to the weight loss according to the reaction:

$$2\ SiO_2\ (l) + SiC\ (s) = 3SiO\ (g) + CO\ (g)\ [23] \quad (1)$$

AlON dissociates into Al_2O_3 and AlN in presence of carbon in a flowing nitrogen gas atmosphere [18].

$$3\ AlON = Al_2O_3 + AlN + N_2 \quad (2)$$

Produced Al_2O_3 then reacts with SiC forming gaseous species Al_2O, SiO and CO resulting into weight loss of the specimens.

$$SiC + Al_2O_3 = Al_2O + SiO + CO\ [23] \quad (3)$$

In this system the sintering was done in a static nitrogen environment under gas pressure (6 bar). Such high nitrogen partial pressure supressed the dissociation of AlON [16] in accordance with the Le Chatelier's principle. Thus, the percent weight loss of the composite in nitrogen atmosphere was independent of γ-AlON content and the general weight loss was comparatively less than that is reported (14.1 wt.%) in the case of pressureless sintering in the similar system [24]. It is further supported by the XRD analysis of the sample sintered in N_2 atmosphere where cubic AlON was found along with cubic solid solution (Fig. 5).

But, when Ar was used, the nitrogen partial partial pressure in the enclosed system became low and it helped to decompose AlON producing AlN and Al_2O_3. The formed Al_2O_3 reacted with SiC to form several volatile products according to the reaction (3). As a result of which the percentage weight loss increased with increase in γ-AlON content. An evidence of reaction (2) was found in the XRD analysis of the sample containing higher amount of γ-AlON (60 wt.% and more), where distinct peak for AlN was identified. But here also, Le Chatelier's principle played an important role to supress the dissociation reaction in a high static gas pressure environment.

Phase analysis by XRD revealed the presence of cubic solid solution as a major one when less than 55 wt.% of γ-AlON was used and sintered in nitrogen atmosphere. Trace amount of 2H and 4H form of SiC was also identified along with γ-AlON. But with increase in γ-AlON in the composition at 60 wt.% and more, hexagonal SiC with AlN was identified. As stated earlier, γ-AlON was stabilised in N_2 atmosphere and helped in formation of cubic solid solution (Fig. 5) and beyond 55 wt.% of γ-AlON enhanced chemical reactivity completely disintegrated the material [Fig. 5(c)]. In the present system hexagoal solid solution emerged as one of the major phases, when the sample was fired in Ar atmosphere (Fig. 5). It is because of the fact that, in Ar atmosphere γ-AlON tend to decompose according to reaction (2) and hexagonal AlN was formed and there are evidences of formation of hexagonal solid solution of SiC with AlN [25,26]. Formation of Al_2OC in the system was not considered as no such phase was found by phase analysis of the sintered specimen.

The above discussions may be summarised as follows:

(a) The hardness of the specimens continuously increased with the increase in γ-AlON content (Fig. 7) up to a certain limit (40–50 wt.% γ-AlON depending on the sintering atmosphere). It should be mentioned here

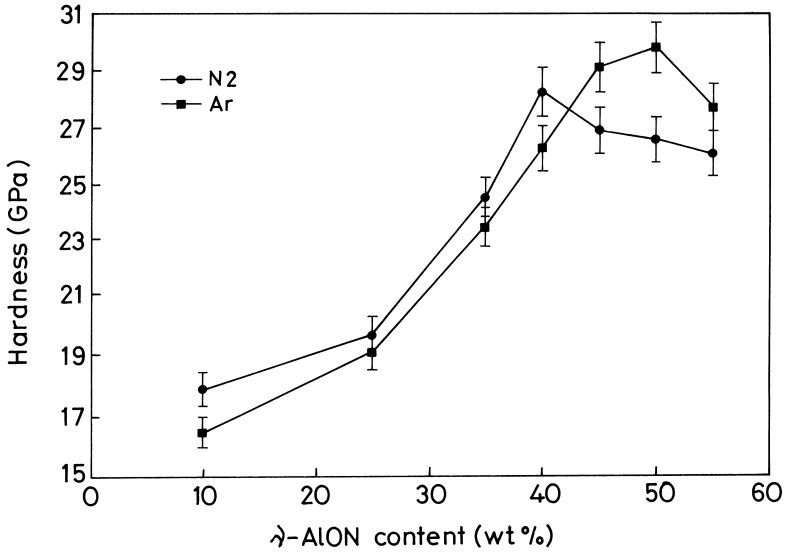

Fig. 7. Plot of microhardness (GPa) of the sample sintered in N_2 and Ar atmosphere with wt.% of γ-AlON content.

that the hardness of sintered γ-AlON is less (18 GPa)[27] than that of sintered SiC (23 GPa) [28].

(b) The *d*-value of silicon carbide of the sintered materials gradually shifted with γ-AlON content. Accordingly the lattice parameter of the composites sintered in N_2 atmosphere at 1950^0C indicated a continuous shifting (Fig. 6).

(c) Measured density was less than the compositional density indicating a change in the chemical composition after sintering.

Thus, it can be concluded that, densification in the SiC-γ-AlON composite system is accompanied by a chemical change producing a solid solution. Therefore, sintering mechanism is likely to be governed by the effective diffusivity of the system. The alternative mechanism of densification by the formation of liquid-phase is not likely in the present system, as the binary Al_2O_3–AlN phase diagram [16] indicates no lquid-phase formation in the system at the sintering temperature (1950°C). The possibility of liquid-phase formation in the aluminosilicate system (small amount of SiO_2 comes from surface oxidation of SiC and Al_2O_3 comes from γ-AlON) is not possible due to a high carbon activity operating in the reaction system under N_2 as well as Ar atmosphere. Hence, it may be said that β-SiC and γ-AlON form a solid solution during densification.

5. Conclusions

β-SiC and γ-AlON are compatible with each other and form a dense composite up to a composition of 55 wt.% of γ-AlON at a temperature of 1950°C in N_2 and Ar atmosphere under a gas pressure of 6 bar. The hardness of the sintered composites was in the range of 16.5–29.8 GPa under a load of 1 N. Solid solution formation during densification was the general feature in both N_2 as well as in Ar atmosphere. A solid state molecular/ionic movement is suggested to be a likely mechanism of densification. In N_2 atmosphere the cubic solid solution was identified as the major phase. But in Ar atmosphere formation of hexagonal solid solution was favoured over cubic solid solution.

Acknowledgements

The authors are grateful to Dr. H.S. Maiti, Director, C.G. & C.R.I. for his valuable suggestions during the work and for his permission to publish the work. Acknowledgement is also due to Dr. D. Chakraborty for carrying out the measurement of hardness of the samples. Acknowledgement is also due to the HRDG, Council of Scientific and Industrial Research for providing financial support.

References

[1] S. Prochazka, Sintering of silicon carbide, in: J.J. Bruke, A.E. Gorum, R.M. Katz (Eds.), Proceedings of the Conference on Ceramics for High Performance Applications, Hyannis, MA, 1973, Brook Hill Publishing, 1975, pp. 239–252.
[2] Q. Tian, A.V. Virkar, Interdiffusion in SiC–AlN and Al_2OC systems, J. Am. Ceram. Soc. 79 (8) (1996) 2168–2174.
[3] W. Rafaniello, K. Cho, A.V. Virkar, Fabrication and characterisation of SiC-AlN alloys, J. Mater. Sci. 16 (1981) 3479–3488.
[4] M.A. Mulla, V.D. Krstic, Low temperature pressureless sintering of β-silicon carbide with aluminium oxide and yttrium oxide addition, Am. Ceram. Soc. Bull. 70 (1991) 439–443.
[5] T. Grande, H. Sommerset, E. Hagen, K. Wiik, M.A. Einarsrud, Effect of weight loss on liquid-phase sintered silicon carbide, J. Am. Ceram. Soc. 80 (4) (1997) 1047–1052.
[6] A.K. Samanta, K.K. Dhargupta, S. Ghatak, SiC–YAG sintered composites from hydroxy-hydrogel powder precursors, Ceram. Int. 26 (2000) 831–838.
[7] S. Ghatak, K.K. Dhargupta, A.K. Samanta. Process for making yttria–alumina–silicon carbide composite useful as engineering ceramics and a process for making components thereof, Patent Applicaton No. 375/Del/98, India.
[8] S. Ghatak, K.K. Dhargupta, S. Mandal, A process for making sintered SiC composites useful as engineering ceramics, Patent Application No. 290/Del/99, India.
[9] S. Ghatak, K.K. Dhargupta, S. Mandal, A process for making sintered silicon carbide–neodymium oxide–aluminium oxide composites, Patent Application No. 1240/Del/99, India.
[10] S. Ghatak, K.K. Dhargupta, S. Mandal, A process for making sintered silicon carbide–praseodymium oxide–aluminium oxide composites, Patent Application No. 1453/Del/99, India.
[11] S. Ghatak, K.K. Dhargupta, S. Mandal, A process for making sintered silicon carbide–lanthanum oxide–aluminium oxide composites. Patent Application No. 1457/Del/99, India.
[12] S. Ghatak, K.K. Dhargupta, S. Mandal, A process of making sintered silicon carbide–samarium oxide–aluminium oxide composites, Patent Application No. 1494/Del/99, India.
[13] Z. Chen, Effect of gadolinia and alumina addition on the densification and toughening of silicon carbide, J. Am. Ceram. Soc. 79 (2) (1996) 530–532.
[14] I.B. Cutler, P.D. Miller, W. Rafaniello, H.K. Pask, D.P. Jack, K.H. Jack, New materials in the Si–C–Al–O–N and related systems, Nature 275 (5679) (1978;434-435.
[15] S.Y. Kuo, Z.C. Jou, A.V. Virkar, W. Rafaniello, Fabrication, thermal treatment and microstructure development in SiC–AlN–Al_2OC ceramics, J. Mater Sci. 21 (1986) 3019–3024.
[16] N.D. Corbin, State of the art aluminium oxynitride spinel: a review, J. Eur. Ceram. Soc. 5 (1989) 143–154.
[17] J.N. McCauley, A simple model for aluminium oxynitride spinels, J. Am. Ceram. Soc. 61 (78) (1978) 372–373.
[18] H.X. Willems, M.M.R.H. Hendrix, R. Metselaar, G. de With, Thermodynamics of AlON. I: Stability at lower temperature, J. Eur. Ceram. Soc. 10 (1992) 327–337.
[19] G. Ado, D. Bernache, M. Billy, K.S. Han, P. Lefort, Mecanisme de frittage sous charge du nitrure d' aluminium et de l'oxynitrure ALON-γ, Revue de Chimie Minerale 22 (1985) 473.
[20] I.U. Kim, V.L. Richards, High-temperature electrical conductivity of aluminium oxynitride spinel, J. Am. Ceram. Soc. 68 (8) (1985) C–120.
[21] E.A. Maguire, T.M. Harnet, R.L. Gentilman, Method of producing aluminium oxynitride having improved optical characteristics, US Patent No. 4520116, 28 May 1985.
[22] S. Ghatak., A.S. Sanyal, K.K. Dhargupta, S. Mandal, An improved process for preparing sintered SiC useful for making industrial products, Patent Application No. 270/Del/99, 19.02.99, India.

[23] T. Grande, H. Sommerset, E. Hagen, K. Wiik, M.A. Einarsrud, Effect of weight loss on liquid phase sintered silicon carbide, J. Am. Ceram. Soc. 80 (4) (1997) 1047–1052.
[24] Lee Jong-Kook, H. Tanaka, H. Kim, Formation of solid solution between SiC and AlN during liquid-phase sintering, Mater. Lett. 29 (1996) 1–6.
[25] A. Zangvil, R. Ruh, Phase relationships in the silicon carbide–aluminium nitride system, J. Am. Ceram. Soc. 71 (10) (1988) 884–890.
[26] E.G. Hilmas, Tseng-Ying Tien, Effect of AlN and Al_2O_3 additions on the phase relationships and morphology of SiC. Part I. Compositions and properties, J. Mater. Sci. 34 (1999) 5605–5612.
[27] G.D. Quinn, N.D. Corbin, J.W. McCauley, Thermomechanical properties of aluminium oxynitride spinel, Ceram. Bull. 63 (5) (1984) 723–730.
[28] M. Shimada, K. Sasaki, M. Koizumi. Fabrication and characterisation of SiC–AlN ceramics by high pressure hot-pressing, in: Proceedings of the International Symposium on Ceramic Components for Engine, Japan, 1983, pp. 466–472.