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Liquid Phase Sintering of Silicon Carbide with AlN-Re_2O_3 Additives

Laner Wu, Yuhong Chen ,Yong Jiang, Youjun Lu and Zhenkun Huang
School of Material Science & Engineering, Beifang University of Nationalities
Ningxia, China

1. Introduction

Silicon carbide can be pressureless sintered by a solid stated process with the sintering aids of B and C to near full density at temperatures in excess of 2100℃(Prochazka,1974). However, the lower fracture toughness (3 to 4 Mpa·$m^{1/2}$) limit their use in many potential structural applications. It has been known that sintering of SiC can be achieved at relatively lower temperature (1850℃-2000℃) with the addition of oxides (Al_2O_3 and Y_2O_3) via liquid phase sintering(Omori & Takei, 1988; Nitin, 1994). The resulting material obtained with homogeneous and equiaxed fine-grained microstructure. Oxides like SiO_2 and Al_2O_3, which are normally considered as thermodynamically stable, are prone to react with SiC at temperature of about 2000℃, leading to formation of gaseous products such as CO, SiO and Al_2O.

$Al_2O_3+SiC \rightarrow Al_2O(g)+SiO(g)+CO(g)$

In order to suppress these reactions, a powder bed is generally required (Tan et al, 1998). Alternatively, the additive system of AlN and rare earth oxides including Y_2O_3, is used where the decomposition of AlN into Al and N_2 can be efficiently controlled by using N_2 atmosphere, leading to lower weight lost (Chia et al, 1994; Ye et al, 20002). The AlN –Y_2O_3 phase diagram indicates that eutectic temperature in this system is about 1850℃ (Kouhik, 2002). It might avoid forming a liquid with rather low melting temperature and a coarse surface of ceramic caused by vaporized gases from the reaction of SiO_2 and Al_2O_3-Y_2O_3. Also in this system the intermediate compositions can offer sufficient amount of liquid with melting temperature higher than 1700℃ as sintering aid of LPS-SiC. Some studies have been carried out by using rare-earth oxide containing densification aids (Koushik et al, 2004; Koushik et al, 2005). Our previous study on melting behaviours of SiC and a series of Re_2O_3 （1∶1 mol mixture）has shown that melting temperatures raise with increasing the atomic number of rare earth element (from La to Er and Y) (Wu et al, 2008). The aim of this work was to study the sintering behavior of liquid phase sintered SiC with AlN and Re_2O_3 (La_2O_3, Nd_2O_3 , Y_2O_3) additive system and their mechanical property in both pressureless sintering and hot press sintering.

2. Material and Method

2.1 Materials

The submicron α-SiC powder was manufactured by Beifang University of Nationalitie. SiC content >97%(mass fraction, the same below), free C<1%, SiO2<1.2%; median particle size of the powder: D_{50} = 0.7μm. AlN powder (D_{50} < 0.8μm, purity>98%) were provided by Beijing Iron Research Institute, Y_2O_3, La_2O_3 and Nd_2O_3 (purity>99.9% D_{50} = 2-5 μm) was provided by Baotou Rear Earth Research Institute. The particle size distribution of the powders was measured by Laser Sizer (model Microtrac X–100, Honeywell, USA). The chemical analysis of the SiC powder was carried out according to Abrasive Grains –chemical analysis of silicon carbide(National Standard of China GB/T 3045-2003) .

2.2 Experimental Methods

2.2.1 Preparation of the powder mixtures

SiC powder and additives were mixed in an attrition mill for about 1 hr in alcohol using Si_3N_4 balls as medium. The compositions of various powder mixtures prepared and the nomenclature used to describe the samples are specified in Table 1. All of the powder mixtures have content of 85% SiC and 15% additives(mass fraction) except "Slay -1". The milled slurry was separated from the milling media and possible wear debris by screening through 320 mesh screen. The slurry was dried in a stirring evaporator and completely dried in a drying oven at 80℃. The dried powder mixture was sieved through 100 mesh.

sample code	AlN /mol%	Y_2O_3 /mol%	Nd_2O_3 /mol%	La_2O_3 /mol%	Theoretical Density ρ/g·cm^{-3}
Sly-1	40	60	0	0	3.40
Sly-2	60	40	0	0	3.38
Sly-3	80	20	0	0	3.34
Sln	60	0	40	0	3.50
Slny	60	20	20	0	3.44
Sla	60	0	0	40	3.47
Slay	60	20	0	20	3.43
Slay-1*	66	17		17	3.45

*Sample " Slay – 1 "has 80% SiC and 20% sintering additives (mass fraction)
Table 1. Compositions and Theoretical Density of powder mixtures

2.2.2 Pressureless Sintering

The mixed powder was axial pressed under pressure of 100Mpa and then cold isostatic pressed under 250 MPa. The rectangular shaped green samples of approximately 10×50×50 mm were sintered in a graphite furnace (made by Robert furnace Co. China). The samples were put into a graphite crucible using BN powder as separator. A high purity N_2 gas atmosphere was used during sintering. The gas pressure was maintained at 0.02 Mpa during sintering. The samples were sintered at 1800, 1850, 1900, 1950, 2000℃ and 2050℃ for

1 hr separately. Heating rates of 20℃/min from ambient temperature to 1600℃ and 10℃ /min from 1600℃ to final sintering temperature were used.

2.2.3 Hot press sintering

The powder mixtures were put in a 40 mm ×40 mm graphite mould (lined with BN powder as separator), hot press sintered under an axial pressure of 30 MPa in N_2 protected atmosphere with a sintering temperature of 1 850 ℃, held for 0.5 h (the furnace made by Shanghai Chenrong Co., China).

2.3 Characterization

The weight loss and linear shrinkage of both green body and sintered specimen of all samples were measured. Bulk density were measured by Archemede's principle by a water displacement method. The hardness was determined by using a load of 98 N in a micro-hardness test fitted with a Vickers square indenter (Wolpert U.S.A). The fracture toughness was calculated by the length of the cracks originating from the edges.: K_{1C}=0.016 (E/Hv)0.5×(p/c-1.5) where K_{1C} is the fracture toughness of the material, Hv is the Vickers hardness, E is the Young's modulus (for LPS-SiC a value of 400 was assumed) c is the crack length(μm) and a is indentation diagonal (Anstis et al, 1981). The specimens were cut into rectangular beams with dimensions of 3×4×36 mm to test three point bending strength. The tensile edges were bevelled to remove stress concentrations and edge flaws caused by sectioning. Observation of the microstructure has been performed by SEM (SSX-550 Shimadzu Japan) on fracture surfaces and also on finished surface polished by 1 μm diamond paste. The phase composition of samples was determined by X-ray diffraction using Cu-Kα radiation (XRD-6000 Shimadzu Japan) , a step width of 0.2 with an exposure time of 2 degree/min per position.

3. Results and discussion

3.1 Sinterability of SiC-AlN-Y_2O_3 system

Similar to other works (Rixecker et al, 2000; Magnani & Beaulardi 2005), the sintering temperature for completed densification is a function of the additive composition and the best densification behavior does not coincide with the eutectic composition in the AlN-Y_2O_3 system(See Fig 1) (Kouhik, 2002), which is about 40 mol% AlN as shown in Fig 2. Sample Sly-2 with 60 mol%AlN reached full density at much lower temperature compared with the other two samples. Further more the temprature range of dentification is much wider than others also. It can be seen obviously that the sample with less AlN content as Sly-1(with 40%AlN) need higher sintering temperature and has very limited adaptive temperature range. Sample Sly-3(with 80%AlN) need even higher sintering temperature, its adaptive sintering temperature range is also very limted. It is well known that an important requirement of liquid phase sintering is that there must be good wetting of the solid phase (SiC) by the liquid phase (additive) and there must be a small contact angle θ between the solid SiC and the liquid drops formed by the additive. R.M.Balestra's work showed that at this additive system with 60%mol% AlN had good wettability (θmin≅6°)(Balestra, et al, 2006).The viscosity of silicate melts increases with their nitrogen content, in analogy to the glass transition temperatures of oxynitride glasses.

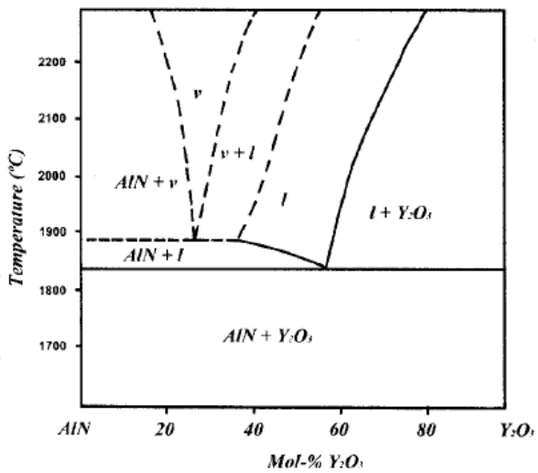

Fig. 1. Phase diagram of the Y_2O_3/AlN system(Kouhik, 2002)

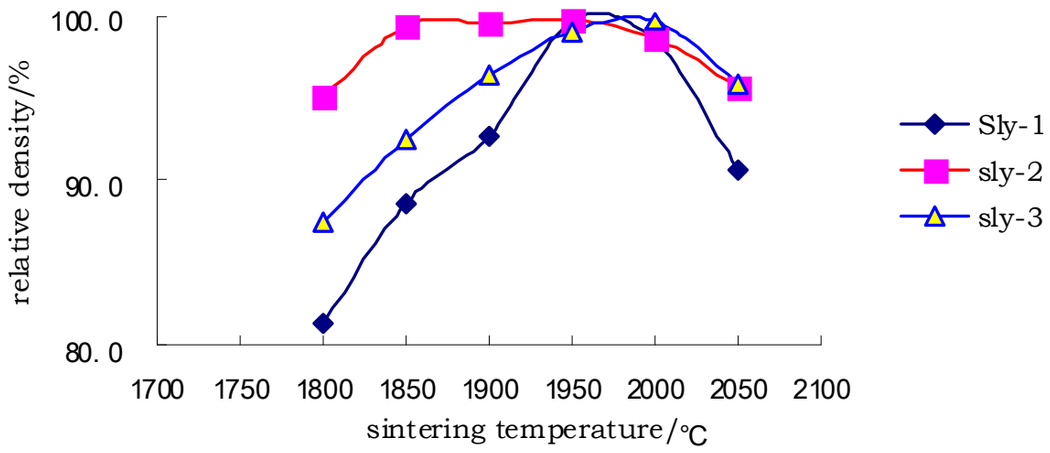

Fig. 2. Sinterable behavior as a function of nitrogen content in the additive

The weight loss of all full density specimens kept about 2%, as shown in Fig 3. When the sintering temperature was raised higher than 2000℃, the weight loss of all specimens increased rapidly up to more than 5%, and the diametric linear shrinkage was less than those in full density temperature. Hence at that temperature, additive decomposition made the density of specimens decrease. It can be seen from Fig. 3 that Sly-1 has less shrinkage than others in the whole temperature range, and less weight loss at lower temperature. Among all samples, Sly-3 has the most even curve both in shrinkage and weight loss . It will bring more convenient sintering process design for densification of SiC. Experimental results showed that SiC-AlN-Y_2O_3 could be fully densified in wide temperature range (1850℃-2000℃), and keep low weight loss around 2% in this range. The surface of specimens remains smooth, indicating that sintering could be done without powder bed.

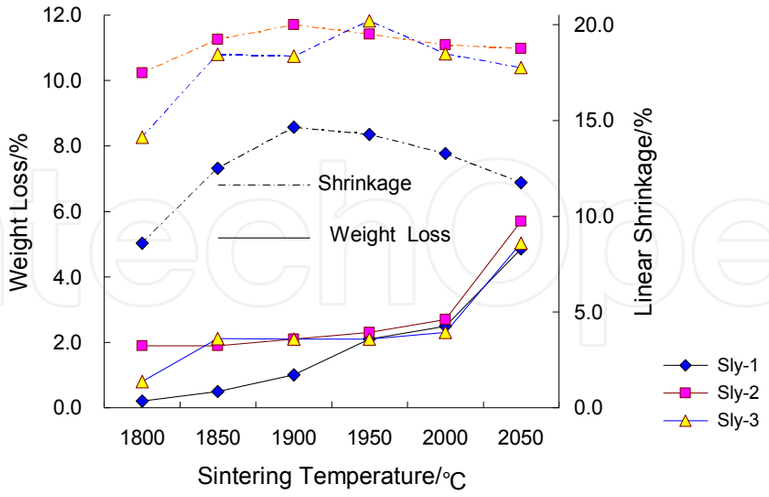

Fig. 3. Weight loss and linear shrinkage of samples VS sintering temperature

It can be seen in the phase diagram of the Y_2O_3/AlN system shown in Fig. 1 that there is a liquid region with sharp lines between the gas(v)/liquid(l) phase region and liquid /Y_2O_3 region. Its eutectic point is near 1 830 ℃(Kouhik, 2002) . The actual sintering temperature is close to the eutectic temperature in order to prevent unfavorable influence of volatilization. The material with the liquid region composition showed less mass loss during high temperature sintering. Experimental results show that SiC-AlN-Y_2O_3 can be fully densified over a wide temperature range (1850℃-2000℃), and keep low weight loss around 2%. The surface of specimens remains smoothly, indicating that sintering could be done without powder bed.

3.2 Sinterability of SiC-AlN-R_2O_3 (R=Nd, La) systems

The best sintered density and corresponding weight loss data of specimens of all test using AlN-Re_2O_3 additive system by using pressureless sintering are shown in Table 2. These test results indicated that the specimens wouldn't been fully densified by using AlN-Nd_2O_3 or AlN-La_2O_3 additive system, all these systems showed much higher weight loss than those results reported in gas pressure sintering (Izhevskyi et al, 2003) which indicated much decomposition reaction occurred without N_2 gas protection.

sample code	Sintering temperature/℃	Weight loss /%	RD ρ/%
Sln	1900	5.9	96.5
Slny	1950	3.1	99.2
Sla	1900	6.9	92.4
Slay	1950	5.1	98.1
Slay-1	1930		97.0
Slay-1 (H P)*	1850		99.3

*Slay-1(HP) was sintered by hot press

Table 2. sintering density and weight loss of AlN- R_2O_3 systems

Interestingly, AlN-Re_2O_3-Y_2O_3 additive system showed much better sintering behaviours than AlN-Re_2O_3 system. Although more weight loss occured than in the AlN- Y_2O_3 system did, and higher sintering temperature was needed for densification.

3.3 Mechanical properties

Mechanical properties of all densified specimens are summarized in Table 3. For AlN-Y_2O_3 system specimens, the hardness (Hv) increased with increasing AlN content. AlN-Nd_2O_3-Y_2O_3 additive specimen show higher hardness than that of all other specimens, which has same hardness as SSSiC(21-25 GPa)(Wu A.,et al,2001). All specimens have bending strength in range of 350-500MPa. All specimens have relative higher fracture toughness compared to SSSiC which is in range of 3-5 MPa·$m^{1/2}$. The SEM picture of crack and the fracture surface are shown in Fig 4. The indicated fracture mode was intergranular fracture. Grain refinement and inter-crystal deflection are the main reasons for the toughness increasing.

sample code	Hardness /GPa	Bending strength/Mpa	Fracture toughness /MPa·$m^{1/2}$
Sly-1	18.7±0.7	410±4.8	6.8±0.4
Sly-2	19.4±0.8	435±42	8.0±0.7
Sly-3	20.8±0.2	481±57	6.1±0.2
Slny	22.2±0.2	--	6.9±0.3
Slay	18.9±1.1	367±13	6.5±0.3
Slay-1	20.5±1.2	434±52	4.8±1.0
Slay-1(HP)	19.0±1.0	828±55	8.6±1.9

Table 3. mechanical properties of best densified specimens

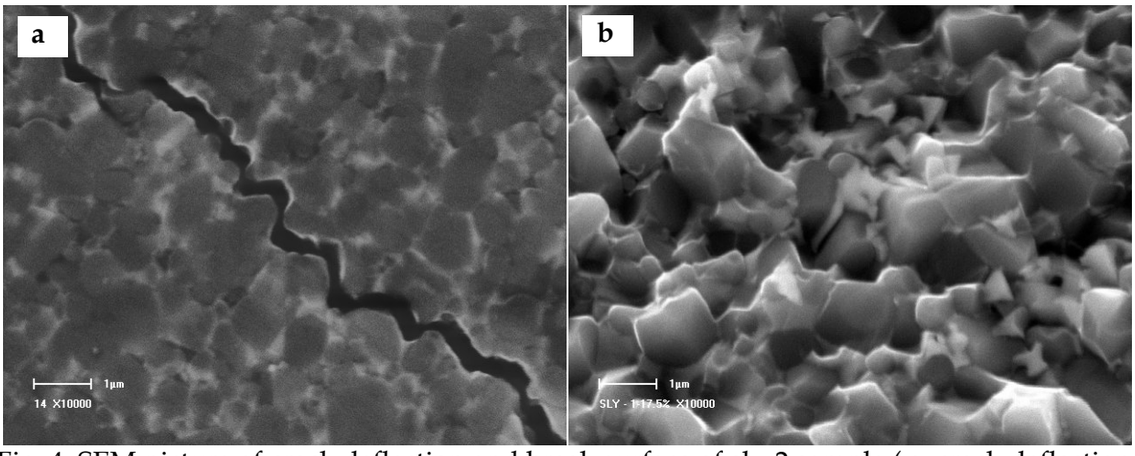

Fig. 4. SEM picture of crack deflection and break surface of sly-2 sample (a. crack deflection, b. fracture surface)

3.4 Microstructure and phase composition

3.4.1 SiC-AlN-Y_2O_3 system

Typical microstructure of AlN-Y_2O_3 system are shown in Fig 5, similar to the microstructure described in previous report(Rixecker G., et al, 2001, Koushik B.,et al, 2005, Wu L., et al, 2008, L.S.Sigl ,2003) . The SiC grains are predominantly equiaxed with a mean grain size of 1-2μm. Relatively little grain growth occurred during densification, indicating that the atomic transport through the melt is sluggish. The core-rim structure is found more clearly in higher AlN content samples.

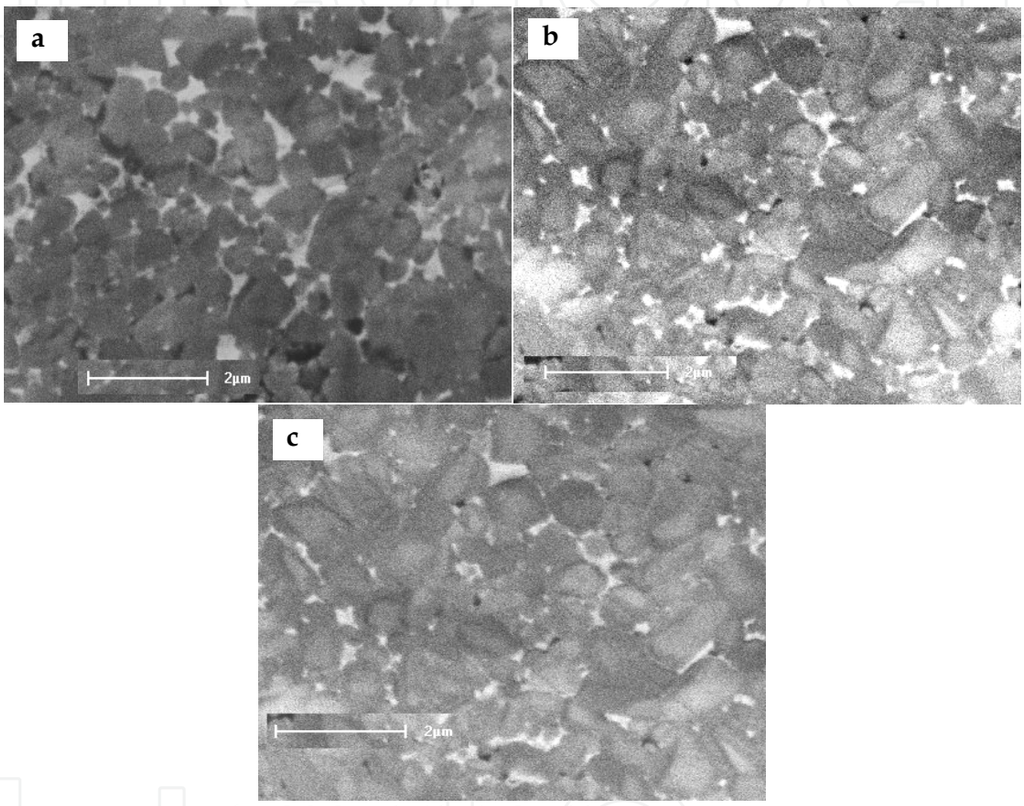

Fig. 5. Microstructure of LPS-SiC with AlN-Y_2O_3 additive
a) sly-1, b) sly-2, c) sly-3

The XRD pattern of the sample is shown in Fig 6. The major phase is 6H - SiC, the minor phases are AlN, Y_2O_3 and $Y_{0.54}Si_{9.57}Al_{2.43}O_{0.81}N_{15.19}$ (α-Sialon). The work of Haihui Ye described that for sample sintered in 1 MPa N_2 atmosphere the AlN, $Y_{10}Al_2Si_3O_{18}N_4$, and $Y_2Si_3N_4O_3$ phase (melilite) were identified; but in Ar , Y_2O_3 and $Y_{10}Al_2Si_3O_{18}N_4$ phase were identified (YE. et al, 2002). Formation of minor $Y_2Si_3N_4O_3$ (melilite) means that a little SiC has been reduced/nitrided to be Si_3N_4 during firing in 1 MPa N_2 atmosphere. In this experiment the nitridation of partial SiC to Si_3N_4 also happened in N_2, 0.02 atm. leading to the formation of $Y_{0.54}Si_{9.57}Al_{2.43}O_{0.81}N_{15.19}$ (α-Sialon), which was from the reaction of the compositions on the one dimension α-Sialon line of Si_3N_4 -Y_2O_3:9AlN with the formula of $YxSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$, x=0.33-0.67(Sigl, 2003). It has been shown that the core-shell

structure which can be seen clearly in Fig 5 formed mainly by solution-reprecipitation of oxynitride or α-Sialon during matter transport.. The subsolidus phase diagram of SiC-AlN-Y_2O_3 system in N_2 is shown in Fig 7.

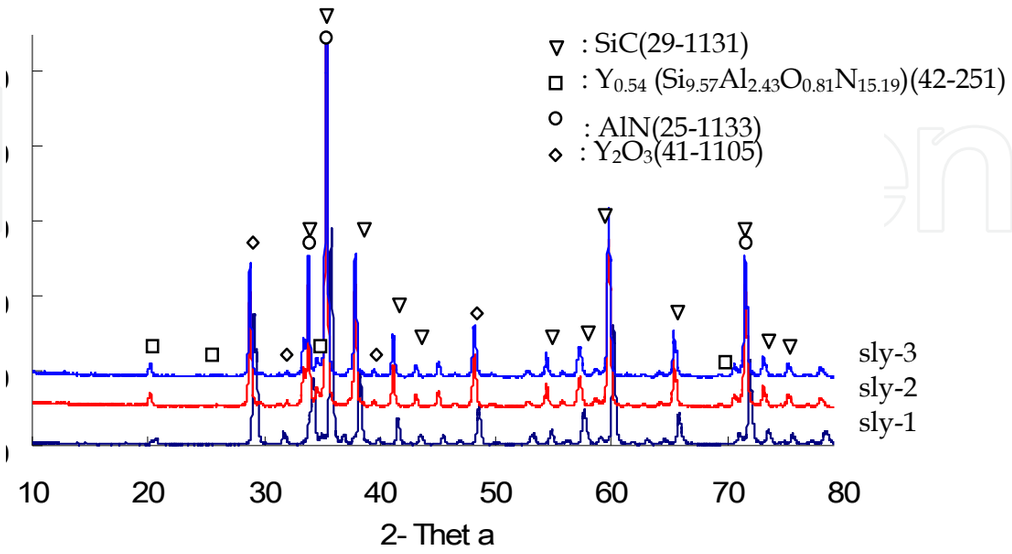

Fig. 6. XRD analysis of sintered sample with AlN-Y_2O_3 additive

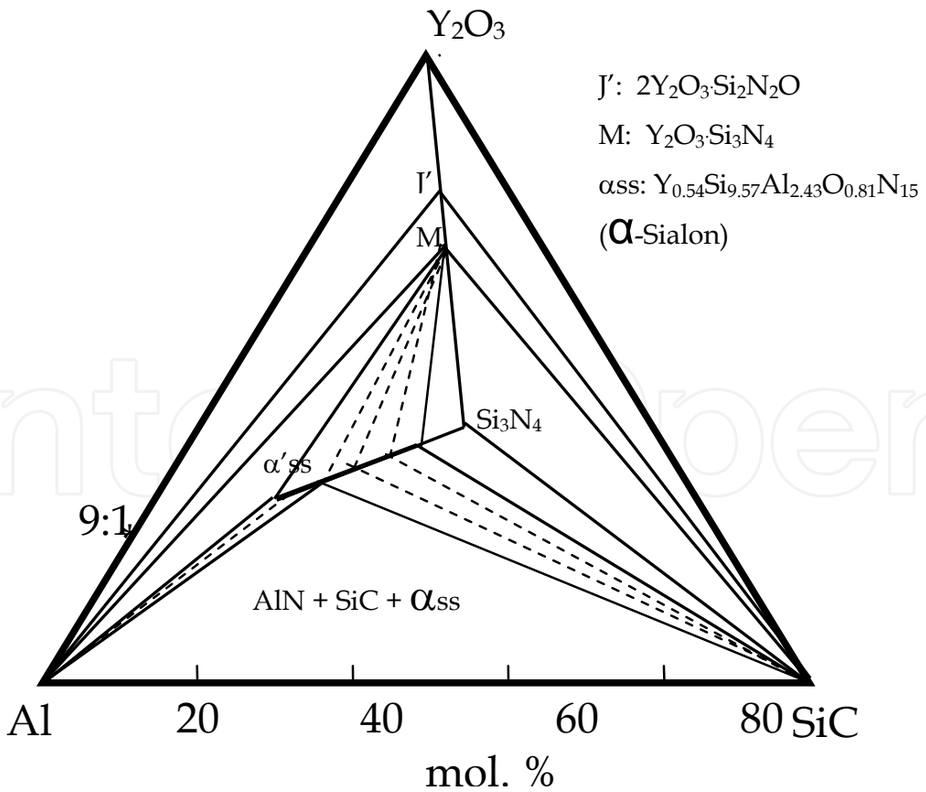

Fig. 7. Subsolidus phase diagram of SiC-AlN-Y_2O_3 system in N_2
* See Huang 1983

3.4.2 SiC-AlN-R_2O_3 (R=Nd, La) systems

For the AlN-Re_2O_3-Y_2O_3 additive system, the microstructure of LPS- SiC is similar to the AlN-Y_2O_3 system, but core-rim structure are hardly found in SEM(Fig 8 a),b),c)). Only in the hot-pressed samples (Fig 8 d)), "core-shell" could be observed obviously. Although the SEM images shown in Fig 8 c) and d) came from the samples with exactly the same composition. The different sintering process bring unlike microstructure of the ceramics. Certainly hot press sintering gains better results. It can be further explained by their mechanical properties.

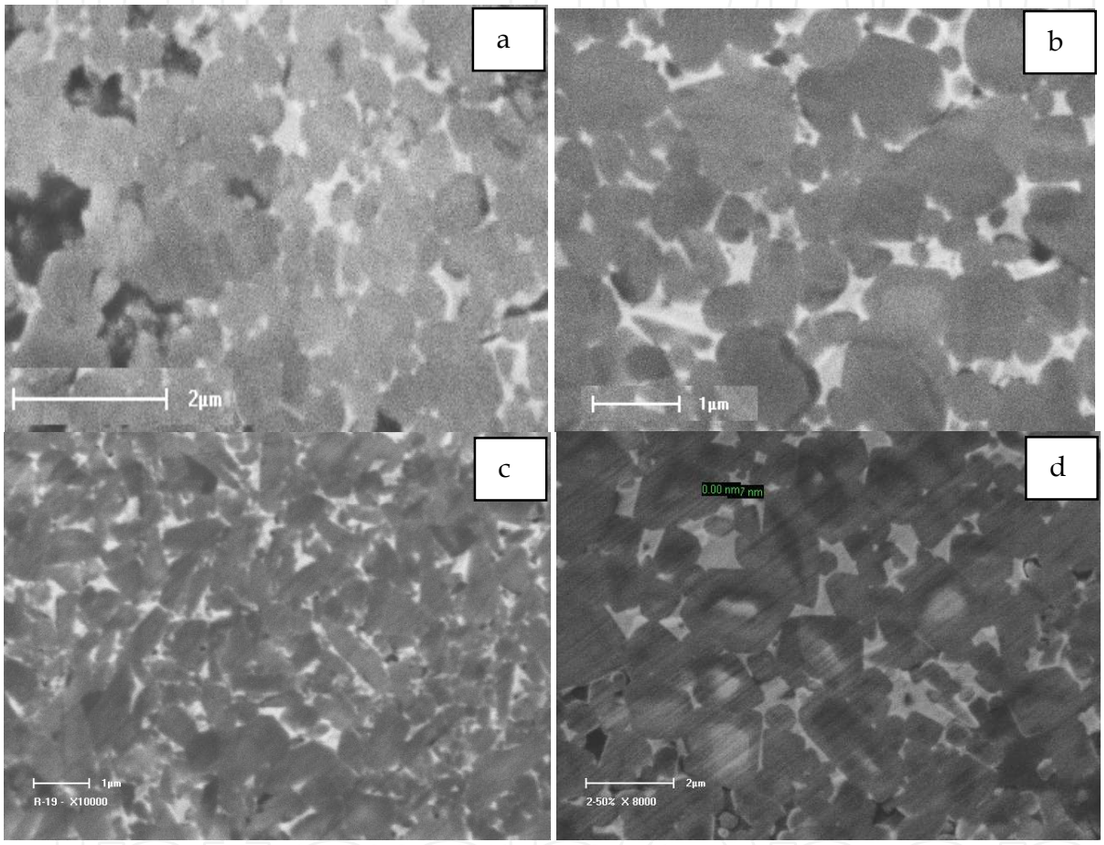

Fig. 8. Microstructure of LPS-SiC with AlN-Re_2O_3 additive
a) slny, b) slay, c) Slay-1, d) Slay-1(HP)

The XRD pattern of the sample with AlN-Nd_2O_3-Y_2O_3 additive is shown in Fig 9, two nitrogen-richer phases of $Y_{0.54}Si_{9.57}Al_{2.43}O_{0.81}N_{15.19}$ (α-Sialon) and $Nd_4Si_2O_7N_2$ (NdAM') were found.

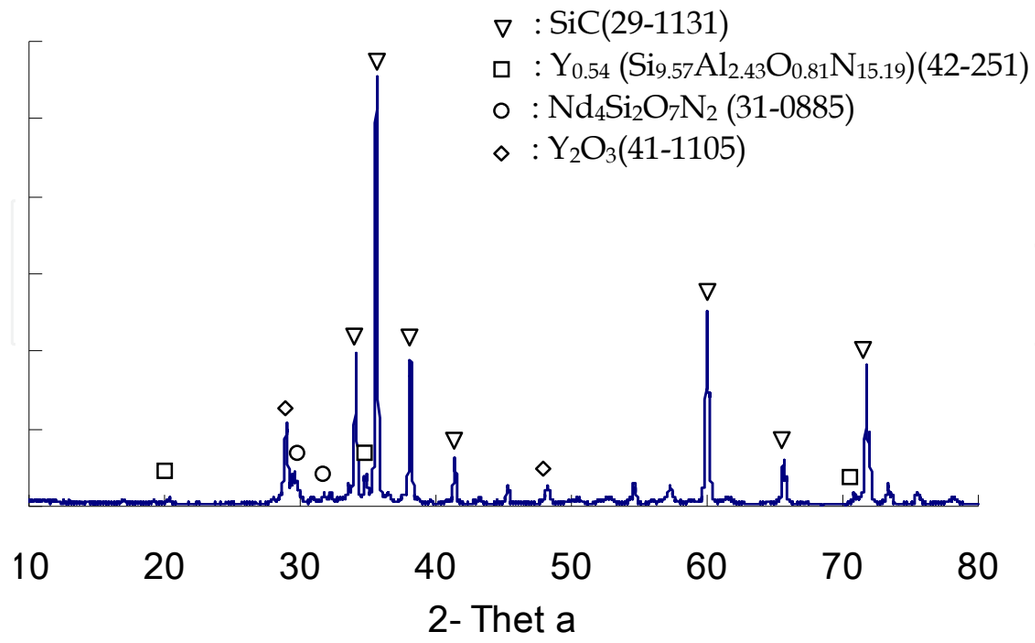

Fig. 9. XRD analysis of sintered sample with AlN-Nd_2O_3-Y_2O_3 additive

4. Conclusion

1. Fully dense SiC ceramics were obtained by liquid phase sintering with AlN-Y_2O_3 and AlN-R_2O_3-Y_2O_3 additives. Materials with 60mol% AlN in AlN-Y_2O_3 additives show that SiC can be sintered over a wide temperature range (1850℃-2000℃), and keeps low weight loss around 2%. The surface of specimens remains smooth, indicating that sintering could be done without powder bed. The specimens made using the AlN-R_2O_3-Y_2O_3 additives systems show higher weight loss, around 5%.
2. The materials obtained have fine-grained and homogeneous microstructure. The core-rim structure can be found in high AlN content specimen. All specimens have higher fracture toughness in the range of 6-8 MPa·$m^{1/2}$. Grain refinement and inter-crystal deflection are the main reasons for toughness increasing. The specimens for AlN-Nd_2O_3-Y_2O_3 additive system showed higher hardness.
3. XRD analysis identified that nitrogen-richer phases of $Y_{0.54}Si_{9.57}Al_{2.43}O_{0.81}N_{15.19}$ (α-Sialon) in AlN-Y_2O_3 additive system and $Nd_2Si_4O_7N_2$ (NdAM′) in AlN-Nd_2O_3-Y_2O_3 additive system formed in the present study, indicating partial SiC was reduced/nitrided to Si_3N_4 or Si_2N_2O.

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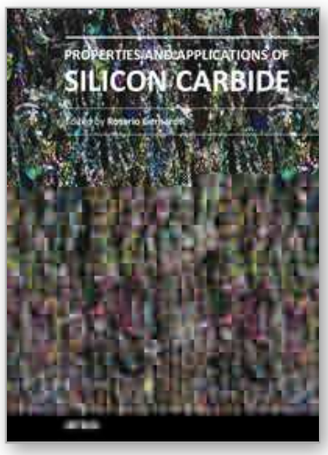

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In this book, we explore an eclectic mix of articles that highlight some new potential applications of SiC and different ways to achieve specific properties. Some articles describe well-established processing methods, while others highlight phase equilibria or machining methods. A resurgence of interest in the structural arena is evident, while new ways to utilize the interesting electromagnetic properties of SiC continue to increase.

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