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# High Temperature Phase Equilibrium of SiC-Based Ceramic Systems

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## 1. Introduction

Silicon carbide (SiC) is one of the promising structure materials for mechanical and thermal applications (Nitin P., 1994). Although SiC ceramic has been developed for several decades, it is still important to study in some areas, ally the high temperature phase relations in SiC-based ceramic systems. In addition, the SiC/Si<sub>3</sub>N<sub>4</sub> composites are of increasing interest because they should have the complement each other in the mechanical properties. (Kim Y. & Mitomo.M, 2000, Lee Y et.al., 2001) SiC and Si<sub>3</sub>N<sub>4</sub> are the strong covalent compounds. The self-diffusion coefficient of Si and C, also Si and N, are too low to get the fully dense ceramics without sintering aids. Rare-earth oxides are often used as liquid phase sintering aids for densification. the behaviours of their high temperature reactions and the derived phase relations are still unknown. Becher (Becher et al, 1996) found that the chemical composition of the grain boundary amorphous phase could significantly influence the interfacial debonding behaviour in silicon nitride. Other study (Keebe H. et.al., 1996) also showed that the secondary phase chemistry could play a key role in toughening Si<sub>3</sub>N<sub>4</sub> ceramic due to its influences on the grain morphology formation, secondary-phase crystallization and residual stress distribution at grain boundaries. For SiC ceramics less of reaction behaviour at high temperature was known due to its sluggish diffusion. About phase relations the Si<sub>3</sub>N<sub>4</sub>-containing systems have been much published (Anna E. McHale. 1994), but either SiC-based ceramic or SiC/ Si<sub>3</sub>N<sub>4</sub> composite systems were rarely done. Even so, the compatibility relations of SiC with neighbour phases should be revealed. Doing so is beneficial to practical use in the manufacture of SiC-based ceramics, as well as SiC/ Si<sub>3</sub>N<sub>4</sub> composites.

The present work focused on the determination of the phase relations in the quaternary systems of SiC- Si<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub>-R<sub>2</sub>O<sub>3</sub> (R=La,Gd,Y) at high temperatures. Lanthanum which has lower atomic number in 17 rare earth elements, as a typical light rare-earth oxide, Gd<sub>2</sub>O<sub>3</sub> as middle and Y<sub>2</sub>O<sub>3</sub> as heavy one with similar property as heavy rare earth oxide were chosen to use in this study. Rare earth oxides used as sintering aids retained in intergranular phases after reaction, which cause strength degradation of the material at high temperature. The investigation of phase relations in this quaternary system will be a summary of work from studies of Si-N-O-R (ANNA E. McHale. (1994)) to Si-C-N-O-R systems. Extensive investigation

for the phase relations and reactives in high temperature is beneficial to practical use in the manufacture of SiC-based ceramics, as well as SiC/ Si<sub>3</sub>N<sub>4</sub> composites.

2. Experimental

The starting powders were α-SiC (H.C.Starck), β- Si<sub>3</sub>N<sub>4</sub> (H.C.Starck), La<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> (R<sub>2</sub>O<sub>3</sub> with 99.9% purity, from Baotou Rare-earth Institute, China). The rare earth oxides were calcined in air at 1200°C for 2h before use.The compositions investigated were restricted to the region bound by the points SiC, Si<sub>3</sub>N<sub>4</sub> and R<sub>2</sub>O<sub>3</sub> (R=La,Gd,Y), but SiO<sub>2</sub> came from in situ oxygen impurity on the surface of powders. Selected compositions were made by mixing the required amounts of the starting powders in agate jar mills with absolute alcohol for 2hr. The dried mixtures were hot-pressed in graphite dies 10 mm in diameter lined with BN in a graphite resistance furnace under a pressure of 30MPa at a subsolidus temperature under a mild flow of Ar, as well as N<sub>2</sub> used for comparison. For the systems SiC-R<sub>2</sub>O<sub>3</sub>, the melting behaviours of SiC and R<sub>2</sub>O<sub>3</sub> (1:1 mole ratio) shown in the table 1. In which the subsolidus temperatures were used as the hot-pressing temperatures for some compositions.

R <sub>2</sub> O <sub>3</sub> :SiC (1:1)		Temperatures (°C)				
R <sub>2</sub> O <sub>3</sub>	1600	1700	1750	1800	1850	1900
La <sub>2</sub> O <sub>3</sub>	not melted	partly melted	melted			
Gd <sub>2</sub> O <sub>3</sub>		not melted	Little melted	partly melted	melted	
Y <sub>2</sub> O <sub>3</sub>		not melted	Little melted	Little melted	partly melted	melted

Table 1. Melting behaviors for R<sub>2</sub>O<sub>3</sub> : SiC (1:1)

The specimens were hot-pressed for 1 to 2 hr in the high temperature region and then cooled at 200°C/min.. End points of hot-pressing were obtained where no further phase change was observed when specimens were heated for longer times. An automatic recording X-ray diffraction with monochromated CuKα radiation was used to scan the samples at a rate of 2°/min.

3. Phase relation of binary subsystem

3.1 Phase relation of R<sub>2</sub>O<sub>3</sub>- Si<sub>3</sub>N<sub>4</sub> subsystem

Table 2 shows the phase relation for different Si<sub>3</sub>N<sub>4</sub>-R<sub>2</sub>O<sub>3</sub> binary subsystems in Ar or N<sub>2</sub> atmosphere respectively.

	Si <sub>3</sub> N <sub>4</sub> - La <sub>2</sub> O <sub>3</sub>	Si <sub>3</sub> N <sub>4</sub> -Gd <sub>2</sub> O <sub>3</sub>	Si <sub>3</sub> N <sub>4</sub> -Y <sub>2</sub> O <sub>3</sub>
Ar	2:1,K,J	M,J	M
N <sub>2</sub>	2:1,K,J,	M,J	M,J

Table 2. phase relation of Si<sub>3</sub>N<sub>4</sub>-R<sub>2</sub>O<sub>3</sub> binary subsystem

In the  $\text{Y}_2\text{O}_3$ -  $\text{Si}_3\text{N}_4$  subsystem  $\text{Y}_2\text{O}_3$ -  $\text{Si}_3\text{N}_4$  melilite(M phase ) was determined after hot-pressing under Ar and  $\text{N}_2$  atmosphere. On the M-  $\text{Y}_2\text{O}_3$  join a richer-oxygen phase,  $2 \text{Y}_2\text{O}_3 \cdot \text{Si}_2\text{N}_2\text{O}$  (J-phase, monocl.) was determined, The binary phase diagram of  $\text{Y}_2\text{O}_3$ -  $\text{Si}_3\text{N}_4$  under 1MPa  $\text{N}_2$  is presented as Fig 1(Huang Z. K. & Tien T. Y.,1996).

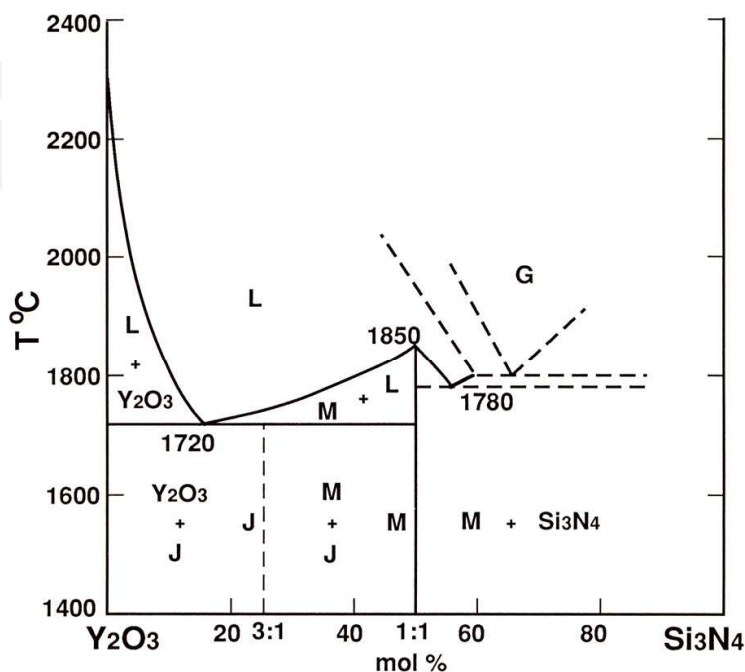
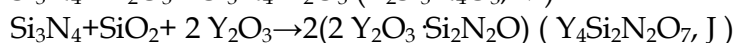
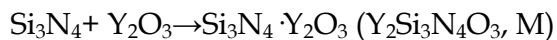
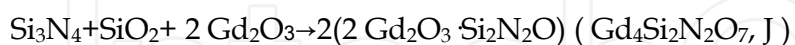
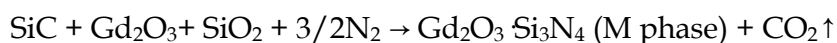


Fig. 1. Phase diagram of  $\text{Y}_2\text{O}_3$ -  $\text{Si}_3\text{N}_4$  subsystem

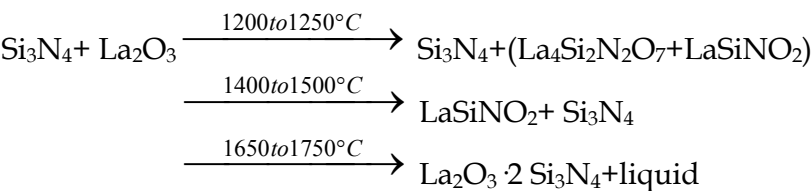
The reaction can be written as follows:



The  $\text{Gd}_2\text{O}_3$ -  $\text{Si}_3\text{N}_4$  subsystem has similar phase relations and reactions.

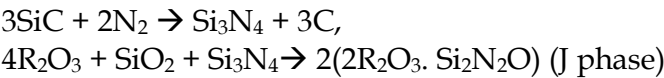


In the  $\text{La}_2\text{O}_3$ -  $\text{Si}_3\text{N}_4$  subsystem  $\text{La}_2\text{O}_3 \cdot 2 \text{Si}_3\text{N}_4$  (monoclinic 2:1) was determined repeatedly after hot-pressing under either Ar or  $\text{N}_2$  atmosphere. A disputed La-melilite ( $\text{La}_2\text{O}_3$ :  $\text{Si}_3\text{N}_4$ ) was not found, because of the large radius of  $\text{La}^{3+}$  ion. It could form only in bigger cell to be  $\text{La}_2\text{O}_3 \cdot \text{Si}_2\text{N}_2\text{O}$ . AlN ( $\text{La}_2\text{Si}_2\text{AlO}_4\text{N}_3$ , melilite) by Al-N replaced for Si-N (Huang Z. K. & Chen I. W.,1996).  $\text{LaSiNO}_2$  (K phase, monoclinic) were determined because of the impurity of powder. On the 2:1-  $\text{La}_2\text{O}_3$  join a richer-oxygen phase,  $2 \text{La}_2\text{O}_3 \cdot \text{Si}_2\text{N}_2\text{O}$  (J-phase, monocl.) was determined, indicating the presence of excess oxygen from  $\text{SiO}_2$  impurity in the powder mixtures. M.Mitomo (Mitomo M.,et.al. 1982)found that an equi-molar mixture of and heated to  $1800^{\circ}\text{C}$  showed that there were three temperature regions in which chemical reaction took place.



3.2 Phase relation of R<sub>2</sub>O<sub>3</sub>-SiC subsystem

No new phase was detected in SiC- Si<sub>3</sub>N<sub>4</sub> and SiC-R<sub>2</sub>O<sub>3</sub> (R=La,Gd,Y) systems, it can be due to its very low self-diffusion coefficient of Si and C with very strong covalence of Si-C bond. However , a few of 2R<sub>2</sub>O<sub>3</sub> Si<sub>2</sub>N<sub>2</sub>O (J phase)was observed in SiC-R<sub>2</sub>O<sub>3</sub> system. The oxygen content of SiC powder, existing either as surface SiO<sub>2</sub> or as interstitial oxygen is between 0.8 to 1.1wt%. The reduction of SiC (lower X-ray peak intensity of SiC) indicated that a part of SiC could directly react with R<sub>2</sub>O<sub>3</sub> after being oxidized/nitrided under N<sub>2</sub>. The reaction can be written as follows:



It should be noted that only a little amount of oxygen content is enough to form much more rare-earth silicon-oxynitrides as shown below: For the examples of La-siliconoxynitrides, one mole of oxygen can cause formation of 2 moles of J phase (La), (Si<sub>2</sub>N<sub>2</sub>O.2La<sub>2</sub>O<sub>3</sub>). It means that 1 wt% O<sub>2</sub> can cause formation of 47.0 wt% J(La) phase.

In fact, it is difficult to make SiC reaction under N<sub>2</sub>, but when rare-earth oxide entered in system, SiC can be reacted even at lower temperature ( 1550°C for SiC- La<sub>2</sub>O<sub>3</sub>, 1600°C for SiC-Gd<sub>2</sub>O<sub>3</sub> system ). The addition of rare-earth oxide benefits the nitride reaction of SiC.

Table 3 shows the phase relation in SiC -R<sub>2</sub>O<sub>3</sub> binary system in different atmosphere.

	SiC- La <sub>2</sub> O <sub>3</sub>	SiC-Gd <sub>2</sub> O <sub>3</sub>	SiC-Y <sub>2</sub> O <sub>3</sub>
Ar	No reaction	No reaction	No reaction
N <sub>2</sub>	J, SiC	J, SiC	J,SiC

Table 3. Formed phase of SiC:R<sub>2</sub>O<sub>3</sub>=1:1 compositions

4. The phase equilibrium of SiC-Si<sub>3</sub>N<sub>4</sub> -R<sub>2</sub>O<sub>3</sub>

The binary phases of La<sub>2</sub>O<sub>3</sub> ·2Si<sub>3</sub>N<sub>4</sub> and Si<sub>3</sub>N<sub>4</sub>.R<sub>2</sub>O<sub>3</sub> (M(Gd),M(Y)) coexist with SiC forming a tie-line which separated every ternary system of SiC- Si<sub>3</sub>N<sub>4</sub>-R<sub>2</sub>O<sub>3</sub> (R=La,Gd,Y) into two triangles, respectively. The 2R<sub>2</sub>O<sub>3</sub> ·Si<sub>2</sub>N<sub>2</sub>O (J phase) also coexist with SiC forming another tie-line in triangle near R<sub>2</sub>O<sub>3</sub> side. Based on the experimental results of binary subsystem, the subsolidus phase diagrams of SiC- Si<sub>3</sub>N<sub>4</sub>-R<sub>2</sub>O<sub>3</sub> (R=La,Gd,Y) systems are presented as Fig. 2.Comparing SiC- Si<sub>3</sub>N<sub>4</sub>-R<sub>2</sub>O<sub>3</sub> with AlN- Si<sub>3</sub>N<sub>4</sub>-R<sub>2</sub>O<sub>3</sub> systems (Cao G.Z., et.al,1989) reported by Cao G.Z. et, the similarity is evident except SiC couldn't participate to form α-Sialon because of its tough Si-C bond with bigger bond length 1.89Å.

The XRD pattern of typical sample after hot-pressed of SiC- Si<sub>3</sub>N<sub>4</sub> -Y<sub>2</sub>O<sub>3</sub> system in N<sub>2</sub> atmosphere is shown in Fig3, phase analysis indicated that M phase (Si<sub>3</sub>N<sub>4</sub> ·Y<sub>2</sub>O<sub>3</sub>), K phase (Si<sub>2</sub>N<sub>2</sub>O ·Y<sub>2</sub>O<sub>3</sub>), or J phase (Si<sub>2</sub>N<sub>2</sub>O ·2Y<sub>2</sub>O<sub>3</sub>) were formed. And in these samples, SiC coexisted with M, K-phase (Fig3-a) , coexisted with Si<sub>3</sub>N<sub>4</sub>, M-phase(Fig3-b) and with Y<sub>2</sub>O<sub>3</sub> ,J phase(Fig3-c). But in sample sintered in Ar atmosphere, K phase had formed instead of J

phase(Fig4). The reason is higher oxygen partial pressure in Ar atmosphere. The introduction of Si<sub>2</sub>N<sub>2</sub>O transformed the ternary system into the quaternary system. In the system, three compatible tetrahedrons, namely, SiC-M-K-J , SiC-M-J-Y<sub>2</sub>O<sub>3</sub> , SiC- Si<sub>3</sub>N<sub>4</sub>-M-K (in N<sub>2</sub>) or SiC- Si<sub>3</sub>N<sub>4</sub>-M-J(in Ar) have been determined. SiC and Si<sub>3</sub>N<sub>4</sub> would selectively equilibrate with these three phases in the order of M < K < J < Y<sub>2</sub>O<sub>3</sub> with respect to the effects of the oxygen content of SiC and Si<sub>3</sub>N<sub>4</sub> powders and the oxygen partial pressure in high temperature. Based on those results, the subsolid phase diagram for the ternary SiC-Si<sub>3</sub>N<sub>4</sub>-Y<sub>2</sub>O<sub>3</sub> system and the quaternary SiC- Si<sub>3</sub>N<sub>4</sub>-Si<sub>2</sub>N<sub>2</sub>O-Y<sub>2</sub>O<sub>3</sub> system are given in Fig 5.

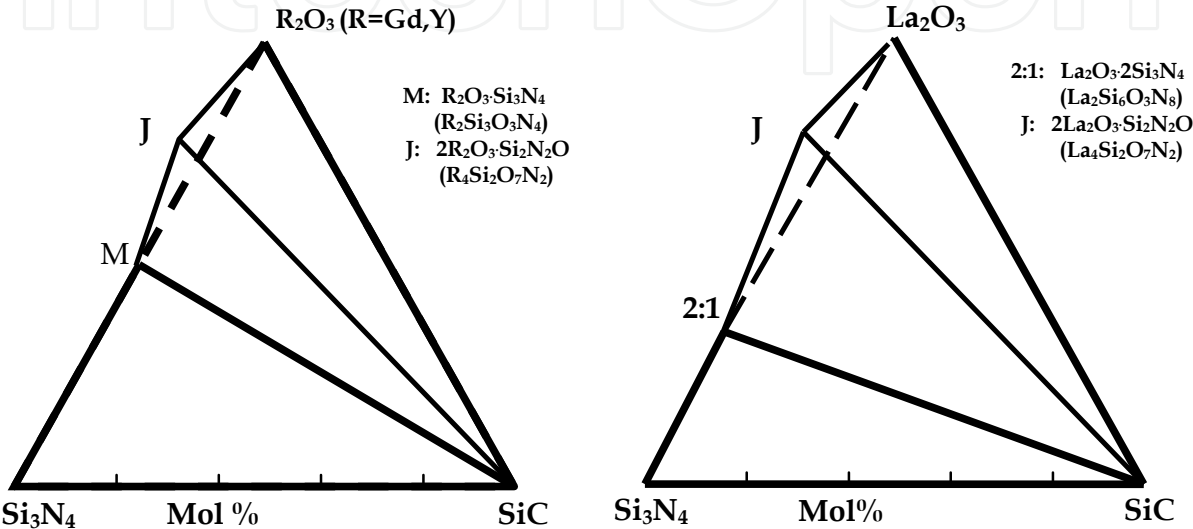


Fig. 2. Subsolidus phase diagram of the system SiC-Si<sub>3</sub>N<sub>4</sub>-R<sub>2</sub>O<sub>3</sub> in Ar or N<sub>2</sub>

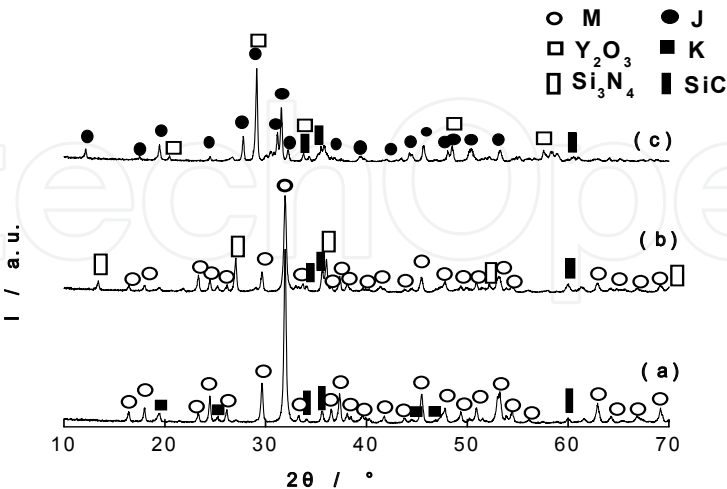


Fig. 3. XRD pattern of SiC-Si<sub>3</sub>N<sub>4</sub>-Y<sub>2</sub>O<sub>3</sub> hot pressed sample in N<sub>2</sub>





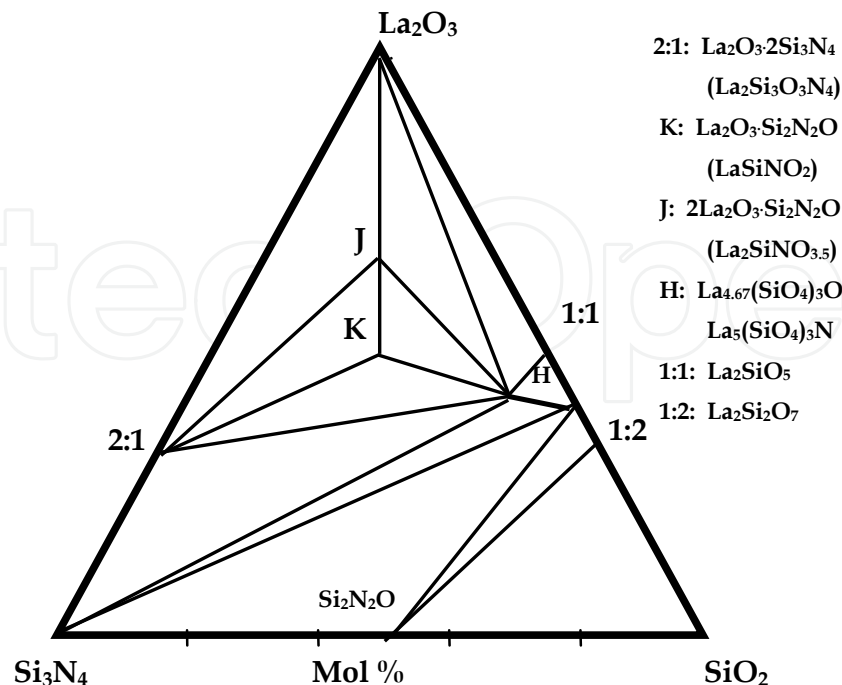


Fig. 7. Subsolidus phase diagram of the system  $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-La}_2\text{O}_3$  in Ar or  $\text{N}_2$ <sup>[9,13]</sup>

As the typical example, Fig 6 showed XRD patterns of four phase coexistence in two typical tetrahedrons respectively in SiC-  $\text{Si}_3\text{N}_4$  - $\text{La}_2\text{O}_3$  system. The oxygen-rich rare-earth silicon-oxynitrides phase  $\text{La}_5(\text{SiO}_4)_3\text{N}$  (H phase) had been indicated in this system. K-phase ( $\text{Si}_2\text{N}_2\text{O} \cdot \text{La}_2\text{O}_3$ )  $2\text{La}_2\text{O}_3 \cdot \text{Si}_2\text{N}_2\text{O}$  (J-phase) were indicated in this system similar with  $\text{Si}_3\text{N}_4$  - $\text{La}_2\text{O}_3$  system, in which J phase also occurred on the binary composition  $\text{Si}_3\text{N}_4:2\text{La}_2\text{O}_3$ . It indicates that the formation of above oxynitrides was related to the presence of excess oxygen from  $\text{SiO}_2$  impurity in the powder mixtures. It should be noted that these oxygen-rich rare-earth silicon-oxynitrides do not lie on the plane SiC-  $\text{Si}_3\text{N}_4$ - $\text{La}_2\text{O}_3$  even so synthesized by these three powders, but lie in the  $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-La}_2\text{O}_3$  system. The isothermal section at  $1700^\circ\text{C}$  of  $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-La}_2\text{O}_3$  system was reported by M.Mitomo(M.Mitomo,1982). Where he obtained J- and K-phase by crystallization from liquid phase, because they lie by a liquid area. In the present work they were obtained directly by solid-state reaction under hot-pressing at  $1550^\circ\text{C}$  and led to construct the subsolidus phase relations of  $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-La}_2\text{O}_3$  system (Fig. 7)( Toropov,et al ,1962, Mitomo,1982) showing some similarity in both. Above all the oxygen-rich rare-earth silicon-oxynitrides and the three members of ternary systems  $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-La}_2\text{O}_3$  were compatible with SiC forming ten four-phase compatibility tetrahedrons as follows:

$\text{SiC-Si}_3\text{N}_4\text{-2:1-H}$ ,  $\text{SiC-Si}_3\text{N}_4\text{-H-Si}_2\text{N}_2\text{O}$ ,  $\text{SiC-H-Si}_2\text{N}_2\text{O-1:2}$ ,  $\text{SiC-Si}_2\text{N}_2\text{O-1:2-SiO}_2$ ,  $\text{SiC-2:1-K-H}$ ,  $\text{SiC-2:1-K-J}$ ,  $\text{SiC-K-J-H}$ ,  $\text{SiC-2:1-J-La}_2\text{O}_3$ ,  $\text{SiC-J-La}_2\text{O}_3\text{-H}$ ,  $\text{SiC-H-La}_2\text{O}_3\text{-1:1}$ .

The subsolidus phase relationship of this quaternary system with ten four-phase compatibility tetrahedrons is plotted in Fig 8.



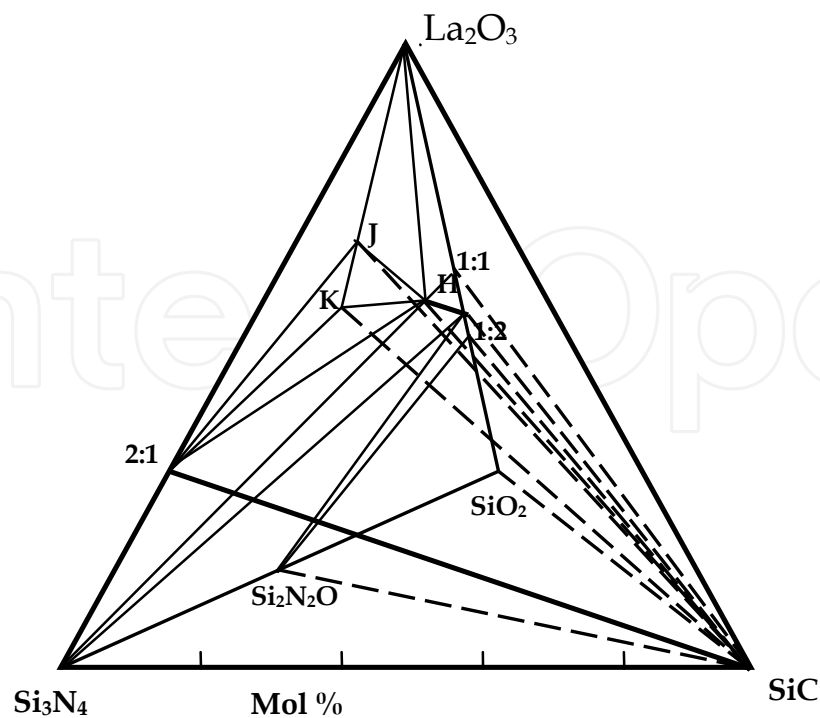


Fig. 8. Subsolidus phase diagram of the system SiC-Si<sub>3</sub>N<sub>4</sub>-La<sub>2</sub>O<sub>3</sub> -SiO<sub>2</sub> in N<sub>2</sub> or Ar

Fig. 8. Subsolidus phase diagram of the system SiC-Si<sub>3</sub>N<sub>4</sub>-La<sub>2</sub>O<sub>3</sub> -SiO<sub>2</sub> in N<sub>2</sub> or Ar  
In the Si<sub>3</sub>N<sub>4</sub>-SiC-Gd<sub>2</sub>O<sub>3</sub> system, the M-phase(Si<sub>3</sub>N<sub>4</sub>·Gd<sub>2</sub>O<sub>3</sub>), J-phase(Si<sub>2</sub>N<sub>2</sub>O·2Gd<sub>2</sub>O<sub>3</sub>) and H-phase ( Gd<sub>10</sub>(SiO<sub>4</sub>)<sub>6</sub>N<sub>2</sub> ) were indicated, a typical XRD pattern of hot-pressure in 1700°C is shown in Fig 9.

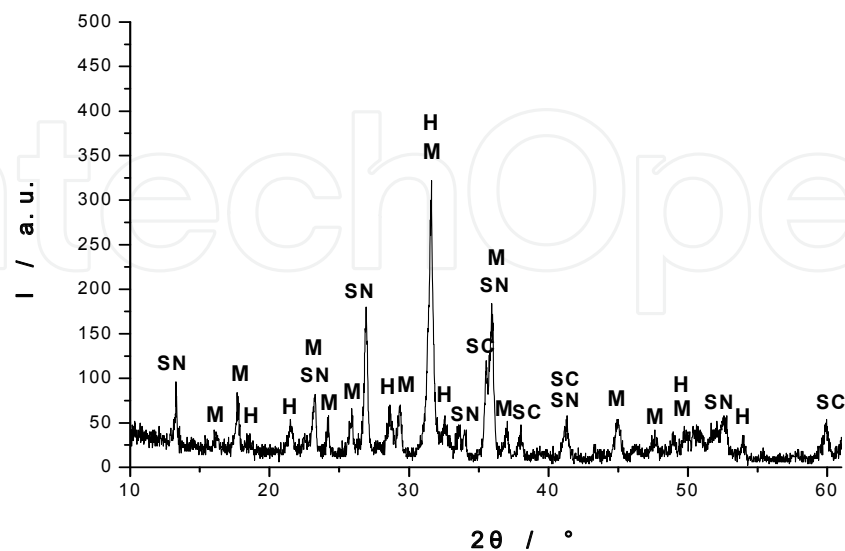


Fig. 9. XRD pattern of SiC-Si<sub>3</sub>N<sub>4</sub>-M(Gd)-H(Gd) four-phases coexistence in the system SiC-Si<sub>3</sub>N<sub>4</sub>-Gd<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>.

Table 4 shows the phase analysis of different compositions in Si<sub>3</sub>N<sub>4</sub>-SiC-Gd<sub>2</sub>O<sub>3</sub> system. With the increasing of SiC and Si<sub>3</sub>N<sub>4</sub>, which means the increasing oxygen content in system, M-phase, J-phase and H-phase would be formed. In the Ar atmosphere, H-phase, which is more oxygen-rich inclined to generation than in N<sub>2</sub> since the higher oxygen particle pressure.

No.	the composition of raw material /mol	Phase composition(in Ar)	Phase composition (in N <sub>2</sub> )
1#	SiC : Si <sub>3</sub> N <sub>4</sub> : Gd <sub>2</sub> O <sub>3</sub> = 4 : 4 : 1	M(vs),Si <sub>3</sub> N <sub>4</sub> (s),SiC(m),H(w)	M(vs), Si <sub>3</sub> N <sub>4</sub> (s), H(m),SiC(w)
2#	SiC : Si <sub>3</sub> N <sub>4</sub> : Gd <sub>2</sub> O <sub>3</sub> = 1 : 1 : 1	M(vs),J(m),SiC(w)	M(vs),J(m),SiC(w)
3#	SiC : Si <sub>3</sub> N <sub>4</sub> : Gd <sub>2</sub> O <sub>3</sub> = 1 : 1 : 2	J(s),H(m),SiC(w)	J(s),SiC(w)
4#	SiC : Si <sub>3</sub> N <sub>4</sub> : Gd <sub>2</sub> O <sub>3</sub> = 1 : 1 : 4	J(s),Gd <sub>2</sub> O <sub>3</sub> (w)	J(vs),SiC(m),Gd <sub>2</sub> O <sub>3</sub> (w)

vs: very strong, s: strong, m: middle w: weak  
Table 4. The compositions of raw material and phase compositions in ternary systems SiC-Si<sub>3</sub>N<sub>4</sub>-Gd<sub>2</sub>O<sub>3</sub> (in Ar or N<sub>2</sub> , 1700°C)

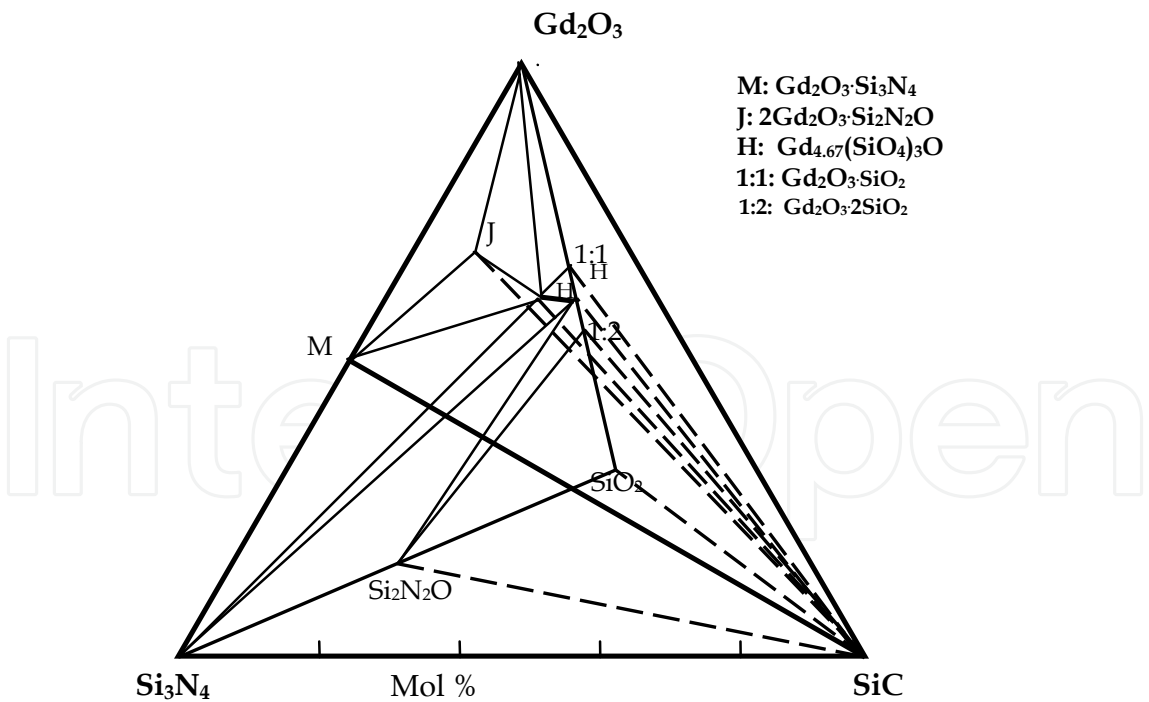


Fig. 10. Subsolidus phase diagram of the system SiC-Si<sub>3</sub>N<sub>4</sub>-Gd<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> in Ar or N<sub>2</sub>

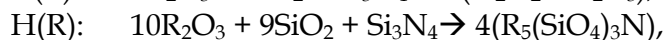
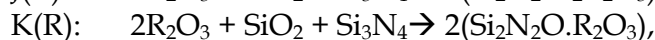
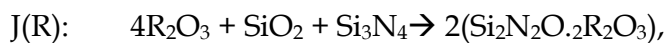
The compositions in the triangles bounded by R-SiC tielines and  $\text{Gd}_2\text{O}_3$  always led to the formation of rare-earth silicon-oxynitrides, indicating the presences of excess oxygen in the powder mixture, that means  $\text{SiO}_2$  in powder also participated in the reaction in the system. Presence of  $\text{SiO}_2$  leads to the quasiternary system  $\text{Si}_3\text{N}_4$ -SiC- $\text{Gd}_2\text{O}_3$  extend into the quaternary system  $\text{Si}_3\text{N}_4$ -SiC- $\text{SiO}_2$ - $\text{Gd}_2\text{O}_3$ . All rare earth silicon-oxinitrides were compatible with SiC, forming eight four-phases compatibility tetrahedrons as follows:

SiC- $\text{Si}_3\text{N}_4$ -M-H, SiC- $\text{Si}_3\text{N}_4$ -H- $\text{Si}_2\text{N}_2\text{O}$ , SiC-H- $\text{Si}_2\text{N}_2\text{O}$ -1:2, SiC- $\text{Si}_2\text{N}_2\text{O}$ -1:2- $\text{SiO}_2$ , SiC-M-J-H, SiC-M-J- $\text{Gd}_2\text{O}_3$ , SiC-J- $\text{Gd}_2\text{O}_3$ -H, SiC-H- $\text{Gd}_2\text{O}_3$ -1:1,

Hence the subsolidus phase diagram of this quaternary system is plotted in Fig. 10.

## 5. The high temperature reaction

Generally, the oxygen content of SiC powder, existing either as surface  $\text{SiO}_2$  or as interstitial oxygen is between 0.8 to 1.1wt%. More than 1.5% of oxygen content exists in  $\text{Si}_3\text{N}_4$  powder. The in-situ  $\text{SiO}_2$  coexisting with powder mixture leads to the quasiternary systems SiC- $\text{Si}_3\text{N}_4$ - $\text{R}_2\text{O}_3$  extend into the quaternary systems SiC- $\text{Si}_3\text{N}_4$ - $\text{SiO}_2$ - $\text{R}_2\text{O}_3$  (R=La,Gd,Y). Just as discussed, only a little amount of oxygen content is enough to form much more rare-earth siliconoxynitrides. That is the reason for easier and much more formation of oxygen-rich rare-earth siliconoxynitrides in the present systems. Their formations are essentially based on the reactions of  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  with  $\text{R}_2\text{O}_3$ , but without  $\text{Si}_2\text{N}_2\text{O}$  presence as following:



The formation of oxygen-rich rare-earth siliconoxynitrides are often accompanied with not only consuming  $\text{Si}_3\text{N}_4$  but also reducing SiC (much lower X-ray peak intensity of SiC) specific when hot-pressing under  $\text{N}_2$  atmosphere. This implies that a part of SiC could also directly react with  $\text{R}_2\text{O}_3$  after being oxidised/nitrided. A few of  $2\text{R}_2\text{O}_3$   $\text{Si}_2\text{N}_2\text{O}$  were observed from SiC- $\text{R}_2\text{O}_3$  binary system when firing in  $\text{N}_2$  atmosphere. In this case the reactions of SiC and  $\text{R}_2\text{O}_3$  can be written as follows:

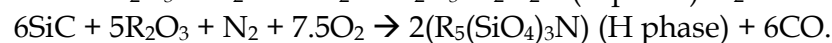
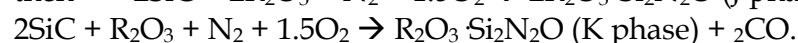
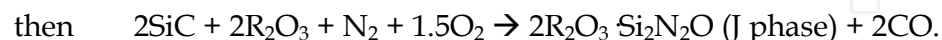
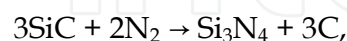
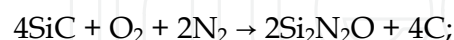
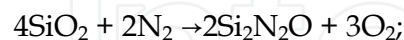
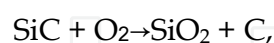


Table 5 summarizes the formation of rare-earth silicon-oxynitrides in the present systems, indicating the trend of formation lessens with decreasing bond ionicity from  $\text{SiO}_2$  to SiC.

	Ionicity	La <sub>2</sub> O <sub>3</sub>	Gd <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>
SiO <sub>2</sub>	5	2:1,H*,1:1	2:1,H*,1:1	2:1,H*,1:1
Si <sub>2</sub> N <sub>2</sub> O	4#	J(1:2),K(1:1),H**	J(1:2),H**	J(1:2) ,K(1:1),H**
Si <sub>3</sub> N <sub>4</sub>	3	2:1	M(1:1)	M(1:1)
SiC (in Ar)	2	No	No	No
SiC (in N <sub>2</sub> )##	2	J	J	J

\*H : R<sub>4,67</sub>(SiO<sub>4</sub>)<sub>3</sub>O.

\*\*H: R<sub>5</sub>(SiO<sub>4</sub>)<sub>3</sub>N or 5R<sub>2</sub>O<sub>3,4</sub>SiO<sub>2</sub>.Si<sub>2</sub>N<sub>2</sub>O.

# Ionicity of Si<sub>2</sub>N<sub>2</sub>O : 5 for Si-O bond, 3 for Si-N bond.

##A few of J phase formed.

Table 5. Formation of some rare-earth siliconoxynitrides (mole ratio)

6. Conclusion

Subsolidus phase diagrams of the ternary systems SiC- Si<sub>3</sub>N<sub>4</sub>-R<sub>2</sub>O<sub>3</sub> (R=La,Gd,Y) were determined. The in-situ SiO<sub>2</sub> impurity in the powder mixtures leads to form some oxygen-rich rare-earth siliconoxynitrides and extend the quasiternary systems into quaternary system of SiC-Si<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub>-R<sub>2</sub>O<sub>3</sub>. The phase relations of these quaternary systems were established with several SiC-containing four-phase compatibility tetrahedrons. The formation of oxygen-rich rare-earth siliconoxynitrides was discussed. When firing under nitrogen atmosphere a part of SiC could also directly tend to react with R<sub>2</sub>O<sub>3</sub> after being oxidised/nitrided forming some rare-earth siliconoxynitrides. They all contributed to construct the phase diagrams of quaternary systems SiC- Si<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub>-R<sub>2</sub>O<sub>3</sub>.

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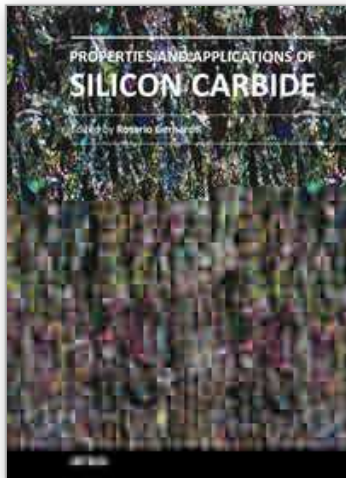
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