We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

High Temperature Phase Equilibrium of SiC-Based Ceramic Systems

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

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/Si₃N₄ 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 Si₃N₄ 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 Si₃N₄ 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 Si₃N₄-containing systems have been much published (Anna E. McHale. 1994), but either SiC-based ceramic or SiC/ Si₃N₄ 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/ Si₃N₄ composites.

The present work focused on the determination of the phase relations in the quaternary systems of SiC- Si₃N₄-SiO₂-R₂O₃ (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, Gd₂O₃ as middle and Y₂O₃ 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/ Si₃N₄ composites.

2. Experimental

The starting powders were α-SiC (H.C.Starck), β- Si₃N₄ (H.C.Starck), La₂O₃, Gd₂O₃ and Y₂O₃ (R₂O₃ 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 poins SiC, Si₃N₄ and R₂O₃ (R=La,Gd,Y), but SiO₂ 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 N₂ used for comparison. For the systems SiC-R₂O₃, the melting behaviours of SiC and R₂O₃ (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 ₂ O ₃ :SiC (1:1)		Temperatures (°C)				
R ₂ O ₃		1600	1700	1750	1800	1850 1900
La ₂ O ₃	not melted	partly melted	melted			
Gd ₂ O ₃		not melted	Little melted	partly melted	melted	
Y ₂ O ₃		not melted	Little melted	Little melted	partly melted	melted

Table 1. Melting behaviors for R₂O₃ : 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 R₂O₃- Si₃N₄ subsystem

Table 2 shows the phase relation for different Si₃N₄-R₂O₃ binary subsystems in Ar or N₂ atmosphere respectively.

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

Table 2. phase relation of Si₃N₄-R₂O₃ binary subsystem

In the Y_2O_3 - Si_3N_4 subsystem Y_2O_3 - Si_3N_4 melilite(M phase) was determined after hot-pressing under Ar and N_2 atmosphere. On the M- Y_2O_3 join a richer-oxygen phase, $2 Y_2O_3 Si_2N_2O$ (J-phase, monocl.) was determined, The binary phase diagram of Y_2O_3 - Si_3N_4 under 1MPa N_2 is presented as Fig 1(Huang Z. K. & Tien T. Y.,1996).

Fig. 1. Phase diagram of Y_2O_3 - Si_3N_4 subsystem

The reaction can be written as follows:

The Gd_2O_3 - Si_3N_4 subsystem has similar phase relations and reactions.

In the La_2O_3 - Si_3N_4 subsystem $La_2O_3 \cdot 2 Si_3N_4$ (monoclinic 2:1) was determined repeatedly after hot-pressing under either Ar or N_2 atmosphere. A disputed La-melilite (La_2O_3 : Si_3N_4) was not found, because of the large radius of La^{3+} ion. It could form only in bigger cell to be $La_2O_3 \cdot Si_2N_2O$. AlN ($La_2Si_2AlO_4N_3$, melilite) by Al-N replaced for Si-N (Huang Z. K. & Chen I. W.,1996). $LaSiNO_2$ (K phase, monoclinic) were determined because of the impurity of powder. On the 2:1- La_2O_3 join a richer-oxygen phase, $2 La_2O_3 Si_2N_2O$ (J-phase, monocl.) was determined, indicating the presence of excess oxygen from 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°C showed that there were three temperature regions in which chemical reaction took place.

phase(Fig4). The reason is higher oxygen partial pressure in Ar atmosphere. The introduction of Si₂N₂O transformed the ternary system into the quaternary system. In the system, three compatible tetrahedrons, namely, SiC-M-K-J , SiC-M-J-Y₂O₃ , SiC- Si₃N₄-M-K (in N₂) or SiC- Si₃N₄-M-J(in Ar) have been determined. SiC and Si₃N₄ would selectively equilibrate with these three phases in the order of M < K < J < Y₂O₃ with respect to the effects of the oxygen content of SiC and Si₃N₄ powders and the oxygen partial pressure in high temperature. Based on those results, the subsolid phase diagram for the ternary SiC-Si₃N₄-Y₂O₃ system and the quaternary SiC- Si₃N₄-Si₂N₂O-Y₂O₃ system are given in Fig 5.

Fig. 2. Subsolidus phase diagram of the system SiC-Si₃N₄-R₂O₃ in Ar or N₂

Fig. 3. XRD pattern of SiC-Si₃N₄-Y₂O₃ hot pressed sample in N₂

Fig. 4. XRD pattern of SiC-Si₃N₄-Y₂O₃ hot pressed sample in Ar

Fig. 5. Subsolidus phase diagram of SiC- Si₃N₄-Si₂N₂O-Y₂O₃ system(a: in N₂,b:in Ar

Fig. 6. XRD pattern of SiC-Si₃N₄-2:1-H showing coexistence of four phases in the system SiC-Si₃N₄-La₂O₃-SiO₂.

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 N_2 ^[9,13]

As the typical example, Fig 6 showed XRD patterns of four phase coexistence in two typical tetrahedrons respectively in SiC- Si_3N_4 - La_2O_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 Si_3N_4 - La_2O_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 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- Si_3N_4 - La_2O_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°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°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:
 $\text{SiC-Si}_3\text{N}_4\text{-2:1-H}$, $\text{SiC-Si}_3\text{N}_4\text{-H-Si}_2\text{N}_2\text{O}$, $\text{SiC-H-Si}_2\text{N}_2\text{O-1:2}$, $\text{SiC-Si}_2\text{N}_2\text{O-1:2-SiO}_2$, SiC-2:1-K-H , SiC-2:1-K-J , 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-Si₃N₄-La₂O₃ -SiO₂ in N₂ or Ar

Fig. 8. Subsolidus phase diagram of the system SiC-Si₃N₄-La₂O₃ -SiO₂ in N₂ or Ar
In the Si₃N₄-SiC-Gd₂O₃ system, the M-phase(Si₃N₄·Gd₂O₃), J-phase(Si₂N₂O·2Gd₂O₃) and H-phase (Gd₁₀(SiO₄)₆N₂) were indicated, a typical XRD pattern of hot-pressure in 1700°C is shown in Fig 9.

Fig. 9. XRD pattern of SiC-Si₃N₄-M(Gd)-H(Gd) four-phases coexistence in the system SiC-Si₃N₄-Gd₂O₃-SiO₂.

Table 4 shows the phase analysis of different compositions in Si₃N₄-SiC-Gd₂O₃ system. With the increasing of SiC and Si₃N₄, 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 N₂ since the higher oxygen particle pressure.

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

vs: very strong, s: strong, m: middle w: weak
Table 4. The compositions of raw material and phase compositions in ternary systems SiC-Si₃N₄-Gd₂O₃ (in Ar or N₂ , 1700°C)

Fig. 10. Subsolidus phase diagram of the system SiC-Si₃N₄-Gd₂O₃-SiO₂ in Ar or N₂

The compositions in the triangles bounded by R-SiC tielines and Gd_2O_3 always led to the formation of rare-earth silicon-oxynitrides, indicating the presences of excess oxygen in the powder mixture, that means SiO_2 in powder also participated in the reaction in the system. Presence of SiO_2 leads to the quasiternary system Si_3N_4 -SiC- Gd_2O_3 extend into the quaternary system Si_3N_4 -SiC- SiO_2 - Gd_2O_3 . All rare earth silicon-oxynitrides were compatible with SiC, forming eight four-phases compatibility tetrahedrons as follows:

SiC- Si_3N_4 -M-H, SiC- Si_3N_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- SiO_2 , SiC-M-J-H, SiC-M-J- Gd_2O_3 , SiC-J- Gd_2O_3 -H, SiC-H- Gd_2O_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 SiO_2 or as interstitial oxygen is between 0.8 to 1.1wt%. More than 1.5% of oxygen content exists in Si_3N_4 powder. The in-situ SiO_2 coexisting with powder mixture leads to the quasiternary systems SiC- Si_3N_4 - R_2O_3 extend into the quaternary systems SiC- Si_3N_4 - SiO_2 - R_2O_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 SiO_2 and Si_3N_4 with R_2O_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 Si_3N_4 but also reducing SiC (much lower X-ray peak intensity of SiC) specific when hot-pressing under N_2 atmosphere. This implies that a part of SiC could also directly react with R_2O_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- R_2O_3 binary system when firing in N_2 atmosphere. In this case the reactions of SiC and R_2O_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 SiO_2 to SiC.

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

*H : R_{4,67}(SiO₄)₃O.

**H: R₅(SiO₄)₃N or 5R₂O_{3,4}SiO₂.Si₂N₂O.

Ionicity of Si₂N₂O : 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- Si₃N₄-R₂O₃ (R=La,Gd,Y) were determined. The in-situ SiO₂ impurity in the powder mixtures leads to form some oxygen-rich rare-earth siliconoxynitrides and extend the quasiternary systems into quaternary system of SiC-Si₃N₄-SiO₂-R₂O₃. 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 R₂O₃ after being oxidised/nitrided forming some rare-earth siliconoxynitrides. They all contributed to construct the phase diagrams of quaternary systems SiC- Si₃N₄-SiO₂-R₂O₃.

Acknowledgements

This study was supported by National Natural Science Foundation of China (50962001). The authors are grateful to Mr. Jiang and Mr. Han for their assistance.

7. References

Nitin P. Padture. (1994)In situ-toughened silicon carbide. J.Am.Ceram.Soc., 1994,77[2]519-523 ISSN :1551-2916

Kim Y. & Mitomo.M . (2000) Fabrication and mechanical properties of silicon carbide-silicon nitride nanocomposites. J. materail Science. 35(2000)5885-5890 ISSN :0022-2461

Lee Y,Kim Y., Choi H., .Lee J.(2001) Effects of additive amount on microstructure and mechanical properties of silicon carbide -silicon nitride composite J. material Science. 36(2001)699-702 ISSN :0022-2461

Becher P.F., Sun Y., Hsueh C., Alexander,K., et..(1996) Debonding of interfaces between beta silicon nitride and Si-Al-Y oxynitride glass Acta Mater., 1996, 44 3881-3893 ISSN :1359-6454

Keeebe H., Pezzotti G., Ziegler G.(1999) Microstructure and fracture toughness of Si₃N₄ ceramics : combined roles of grain morphology and secondary phase chemistry J.Am. Ceram. Soc., 1999, 82,1642-1644 ISSN :1551-2916

- Anna E. McHale. (1994) Phase Diagrams for Ceramists[M]. Vol. X. Compiled at National Inst. of Standards and Techn. Edited and Published by The American Ceramic Society, 36-115. ISBN:0-944904-74-2
- Huang Z. K. & Tien T. Y.(1996) Soli-liquid reaction in the $\text{Si}_3\text{N}_4\text{-AlN-Y}_2\text{O}_3$ system J. Am. Ceram. Soc., 1996, 79[6], 1717-1719. ISSN :1551-2916
- Huang Z. K. & Chen I. W.(1996) Rare-earth melilite solid solution and its phase relations with neigh-boring phase J. Am. Ceram. Soc., 1996, 79 [8] 2091-2097. ISSN :1551-2916
- Mitomo M., Izumi F., Horiuchi S., Matsui Y.. (1982)Phase relationships in the system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-La}_2\text{O}_3$ (1982) J. Of Mater. Sci., 1982,17, 2359-2364 ISSN :0022-2461
- Jack K.H., (1978)Mater. Sci.Res. 1978,11,561-578
- Cao G.Z., Huang Z.K., Yan D.S.. (1989) Phase relationships in $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3$ system. the Science China, Ser.A. 1989 32,4, 429-433 ISSN:1674-7216
- Yan D.S., Sun W.Y. (2000) phase relationship and material design in the Ln-Si-Al-O-N system. Science in China ,series B, 2000, 6 ,225-232 ISSN:1674-7224
- N.A.Toropov,I.A.Bondar F.Ya.Galakhov. Trans. Inter.Ceram. Congr. 8th, Copenhagen Denmark, 1962. 87-90
- Harue Wada, Ming-Jong Wang, and Tseng-Ying Tien, (1988) J. Am. Ceram. Soc.,1998, 71 [10] 837-840.

IntechOpen

Properties and Applications of Silicon Carbide

Edited by Prof. Rosario Gerhardt

ISBN 978-953-307-201-2

Hard cover, 536 pages

Publisher InTech

Published online 04, April, 2011

Published in print edition April, 2011

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.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Yuhong Chen, Laner Wu ,Wenzhou Sun, Youjun Lu and Zhenkun Huang (2011). High Temperature Phase Equilibrium of SiC-Based Materials, Properties and Applications of Silicon Carbide, Prof. Rosario Gerhardt (Ed.), ISBN: 978-953-307-201-2, InTech, Available from: <http://www.intechopen.com/books/properties-and-applications-of-silicon-carbide/high-temperature-phase-equilibrium-of-sic-based-materials>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](https://creativecommons.org/licenses/by-nc-sa/3.0/), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen