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High temperature phase equilibrium of SiC-based ceramic systems: SiC–Si_3N_4–R_2O_3 (R = Gd, Y) systems

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Abstract The phase relations of the ternary systems SiC–Si_3N_4–R_2O_3 (R = Gd and Y) have been investigated by XRD phase analyses of the hot-pressed samples from SiC, Si_3N_4, and R_2O_3 powders. Their subsolidus phase diagrams were presented. In situ SiO_2 impurity in the powders always led to form some oxygen-richer rare-earth siliconoxynitrides and extend the ternary systems to the quaternary systems of SiC–Si_3N_4–SiO_2–R_2O_3 (R = Gd, Y). Within these systems all rare-earth siliconoxynitrides coexist with SiC. The phase diagrams of the quaternary systems of SiC–Si_3N_4–SiO_2–R_2O_3 (R = Gd, Y) were established, in which the subsolidus diagram of Si_3N_4–SiO_2–Gd_2O_3 system was first reported.

Introduction

Present work is a part of our project of studying the phase relations in SiC-based ceramic systems. As well known SiC is strong covalent compound and very sluggish to be sintered. Rare-earth oxides are always used as sintering aids for the densification of SiC ceramics, as well as SiC/Si_3N_4 composites [1–4], but few data of the phase relations exist for SiC ceramic systems. Unlike Si_3N_4 (Sialon) systems which have been much published [5], the reactions at high temperature and then derived the phase relations in either SiC ceramic or SiC/Si_3N_4 composite systems are still indistinct, but should be revealed.

The phase relations of Si_3N_4–R_2O_3 systems have been reported [6–12], involving a series of rare-earth melilite (denoted as M(R)) and an oxygen-richer rare-earth siliconoxynitride (denoted as J(R)) formation. SiC/Si_3N_4 matrix composites could be sintered showing both phases coexist in SiC–Si_3N_4 system [13, 14]. For the systems SiC–R_2O_3 (R = Gd and Y) the phase relations of SiC–Gd_2O_3 system is unknown, but SiC–Y_2O_3 was compatible [15]. The phase diagram of SiC–SiO_2–Y_2O_3 system at 1650 °C has been reported by thermodynamic calculations [15]. Within this system SiC was compatible with Y_2SiO_5 and $Y_2Si_2O_7$, as well as with both members Y_2O_3 and SiO_2.

Present work studies the phase relations of SiC–Si_3N_4–R_2O_3 (R = Gd and Y) systems by solid-state reactions at high temperatures.

Understanding the phase equilibria of SiC, Si_3N_4, and SiC/Si_3N_4 with R_2O_3 (R = Gd and Y) at high temperatures will be beneficial to liquid phase sintering of SiC- and SiC/Si_3N_4-based ceramics. It will also improve the scientific understanding of the factors that control the equilibria of these complex SiC–Si_3N_4–R_2O_3 systems.

Experimental procedure

The starting powders were β-SiC (Grade UF-15-A, H.C. Starck, Chemical composition: C 29.0–30.0%; O max. 1.50%; Al max. 0.03%; Ca max. 0.01%; Fe max. 0.05%, particle size: D50 = 0.55 μm), α-Si_3N_4 (Grade M11, H.C. Starck, Chemical composition: N min. 38.5%; C max. 0.2%; O max. 1.5%; Al max. 0.005%, particle size:D50 = 0.6 μm), Gd_2O_3 and Y_2O_3 (R_2O_3 with 99.9% purity, from Baotou Rare-earth Institute, China). The compositions investigated were restricted to the region bound by the points SiC, Si_3N_4, and R_2O_3 (R = Gd and Y). Selected

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Table 1 Observation of subsolidus temperature and melting point for R_2O_3:SiC (1:1) compositions under an atm. Ar

R_2O_3:SiC (1:1)	Temperatures (°C)					
R_2O_3	1600	1700	1750	1800	1850	1900
La_2O_3	Not melted	Partly melted	Melted			
Gd_2O_3	Not melted	Not melted	Little melted	Partly melted	Melted	
Y_2O_3	Not melted	Not melted	Little melted	Little melted	Partly melted	Melted

compositions were made by mixing the required amounts of the starting powders in agate jar mills with analytical reagent alcohol (with 99.9% purity) for 2 h. 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 30 MPa at a subsolidus temperature under an atmosphere of Ar, as well as N_2 used as a comparison. We observed the melting behaviors of SiC:R_2O_3 = 1:1 (mole ratio) compositions shown in Table 1. The subsolidus temperature (before liquid appearance) ~1700 °C was referred to as a reference of hot-pressing temperatures. All compositions of either binary or ternary systems were hot-pressed at/or below the subsolidus temperature (~1700 °C) in order to obtain the samples reached subsolidus phase equilibria. The specimens were hot-pressed for 1–2 h and then cooled at 200 °C/min in the high temperature region from hot-pressing temperature to 1000 °C and then freely down to room temperature. End points of hot-pressing were obtained where no further phase change was observed when specimens were heated for longer times. Samples that underwent <2% weight loss on the firing were considered in deriving the phase relations. An automatic recording instrument for X-ray diffraction with monochromated Cu Kα radiation was used to scan the samples. The measurement conditions were scan range: 10–80 degrees; scan mode: continuous scan; scan speed: 2°/min; sampling pitch: 0.02°; voltage: 40.0 kV; current: 30.0 mA.

Results and discussion

In present ternary systems SiC–Si_3N_4–R_2O_3 (R = Gd and Y), only a tetragonal melilite on the R_2O_3–Si_3N_4 binary systems: $Gd_2O_3 \cdot Si_3N_4$ (M(Gd)) on Gd_2O_3–Si_3N_4 subsystem, and $Y_2O_3 \cdot Si_3N_4$ (M(Y)) on Y_2O_3–Si_3N_4 subsystem, was identified again. In addition, on the M–R_2O_3 subsystem the composition $3R_2O_3$:Si_3N_4 often formed oxygen-richer siliconoxynitrides, 3/2($2R_2O_3 \cdot Si_2N_2O$) (J(Gd)) and (J(Y)). They do not lie on the R_2O_3–Si_3N_4 binary systems, but lie in the Si_2N_2O-containing systems. These results are the same as those in previous works [6–12]. Above rare-earth siliconoxynitrides were compatible with SiC joining a tie-line, respectively. Not new phase was formed on SiC–Si_3N_4 and SiC–R_2O_3 subsystems. The subsolidus phase diagrams of both ternary systems SiC–Si_3N_4–R_2O_3 (R = Gd and Y) were drawn in Fig. 1. Comparing with Si_3N_4–AlN–R_2O_3 systems reported by one of our authors [9, 10], the similarity is evident except SiC could not participate to form α-Sialon because of its tough Si–C bond with bigger bond length 1.89 Å.

The compositions in the triangles bounded by M(R)–SiC joins and R_2O_3 always led to the formation of some oxygen-richer rare-earth siliconoxynitrides including $2R_2O_3 \cdot Si_2N_2O$ (J, YAM-type oxynitride), $R_2O_3 \cdot Si_2N_2O$ (K, wollastonite), and $R_5(SiO_4)_3N$ (H, Apatite) [6–10], indicating the presence of excess oxygen in the powder mixtures, that means SiO_2 impurity in powders also participated the reaction in the systems. It should be noted that these rare-earth siliconoxynitrides do not lie on the plane SiC–Si_3N_4–R_2O_3 (R = Gd and Y) investigated, but lie in the Si_3N_4–SiO_2–R_2O_3 (R = Gd and Y) systems [6–8]. The subsolidus phase diagram of Si_3N_4–SiO_2–Gd_2O_3 system was first time presented as Fig. 2. It shows something difference in between. That is $R_2O_3 \cdot Si_2N_2O$ (K-phase) formed only in Si_3N_4–SiO_2–Y_2O_3 system, but not formed in Si_3N_4–SiO_2–Gd_2O_3 system.

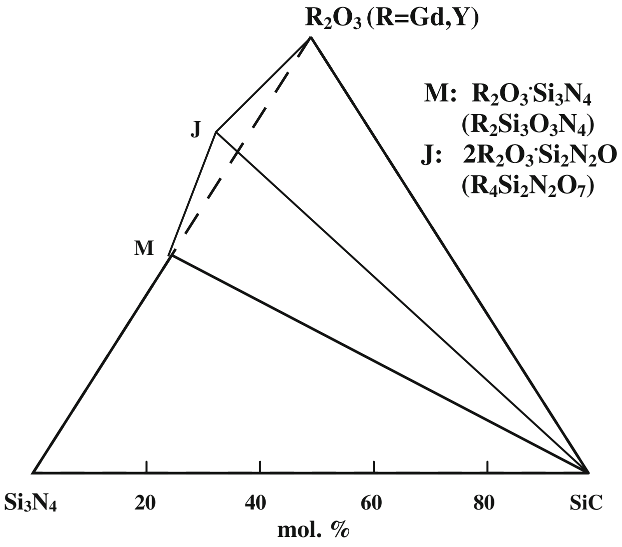

Fig. 1 Subsolidus diagram for the Si_3N_4–SiC–R_2O_3 system

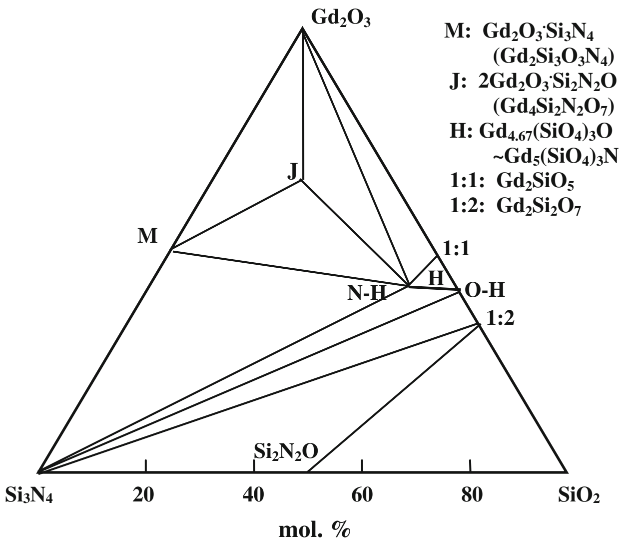

Fig. 2 Subsolidus diagram for the Si_3N_4–SiO_2–Gd_2O_3 system

Table 2 Formation of some rare-earth siliconoxynitrides (mole ratio)

	Ionicity	La_2O_3	Gd_2O_3	Y_2O_3
SiO_2	5	2:1, H[c], 1:1	2:1, H[c], 1:1	2:1, H[c], 1:1
Si_2N_2O	4[b]	J(1:2), K(1:1), H[d]	J(1:2), H[d]	J(1:2), K(1:1), H[d]
Si_3N_4	3	2:1	M(1:1)	M(1:1)
SiC (in Ar)	2	No	No	No
SiC (in N_2)[a]	2	J	J	J

[a] A few of J phase formed

[b] Ionicity of Si_2N_2O: 5 for Si–O bond, 3 for Si–N bond

[c] H: $R_{4.67}(SiO_4)_3O$

[d] H: $R_5(SiO_4)_3N$ or $5R_2O_3{\cdot}4SiO_2{\cdot}Si_2N_2O$

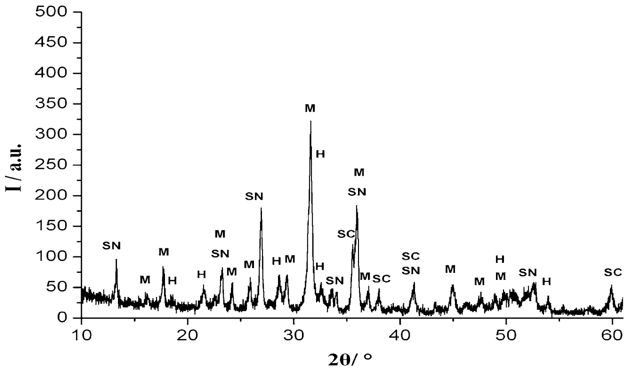

Fig. 3 XRD pattern of $SiC{:}Si_3N_4{:}Gd_2O_3 = 4{:}4{:}1$ composition hot-pressed at 1700 °C. (*SC: SiC, SN: Si_3N, M: $Si_3N_4{\cdot}Gd_2O_3$, H: $Gd_5(SiO_4)_3N$)

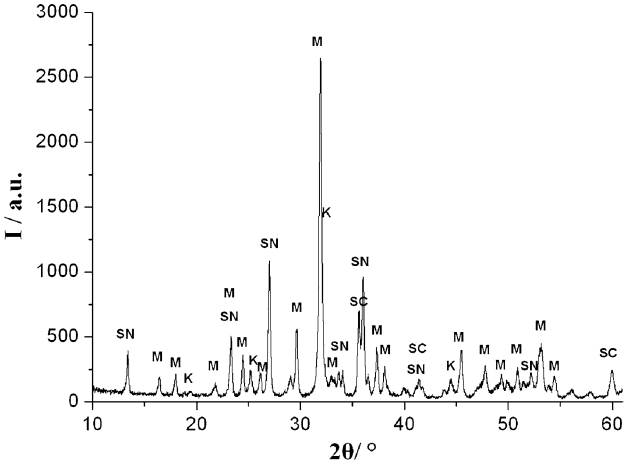

Fig. 4 XRD pattern of $SiC{:}Si_3N_4{:}Y_2O_3 = 3.5{:}3.5{:}1$ composition hot-pressed at 1700 °C. (*SC: SiC, SN: Si_3N_4, M: $Si_3N_4{\cdot}Y_2O_3$, K: $Y_2O_3{\cdot}Si_2N_2O$)

Formation of oxygen-richer rare-earth siliconoxynitrides often accompany with reducing SiC (lower X-ray peak intensity of SiC) specifically when firing under N_2 atmosphere. It indicates that partial SiC could also directly react with R_2O_3 after being oxidized/nitrided by atmosphere.

Table 2 compares the formation of rare-earth siliconoxynitrides in present systems, showing the trend of formation lessens with decreasing bond ionicity from SiO_2 to SiC.

Presence of in situ SiO_2 leads to extend the quasiternary systems SiC–Si_3N_4–R_2O_3 into the quaternary systems SiC–Si_3N_4–SiO_2–R_2O_3 (R = Gd and Y). In these two quaternary systems all of rare-earth siliconoxynitrides were compatible with SiC, forming 84 phases compatibility tetrahedrons for Gd-containing system and 10 for Y-system, as following:

for Gd-containing system,

$SiC-Si_3N_4-M-H$, $SiC-Si_3N_4-H\text{-}1{:}2$, $SiC-Si_3N_4\text{-}1{:}2\text{-}Si_2N_2O$, $SiC-Si_2N_2O\text{-}1{:}2\text{-}SiO_2$,
$SiC-M-H\text{-}1{:}1$, $SiC-M-J\text{-}1{:}1$, $SiC-M-J-Gd_2O_3$,
$SiC-J-Gd_2O_3\text{-}1{:}1$,

for Y-containing system,

$SiC-Si_3N_4-M-K$, $SiC-Si_3N_4-K-H$, $SiC-Si_3N_4-H\text{-}1{:}2$,
$SiC-Si_3N_4\text{-}1{:}2\text{-}Si_2N_2O$, $SiC-Si_2N_2O\text{-}1{:}2\text{-}SiO_2$,
$SiC-M-K-J$, $SiC-M-J-Y_2O_3$, $SiC-J-Y_2O_3\text{-}1{:}1$,
$SiC-J\text{-}1{:}1\text{-}K$, $SiC\text{-}1{:}1\text{-}K-H$.

As typical examples Figs. 3 and 4 show XRD patterns of four phases coexistence in a typical tetrahedron in Gd- and

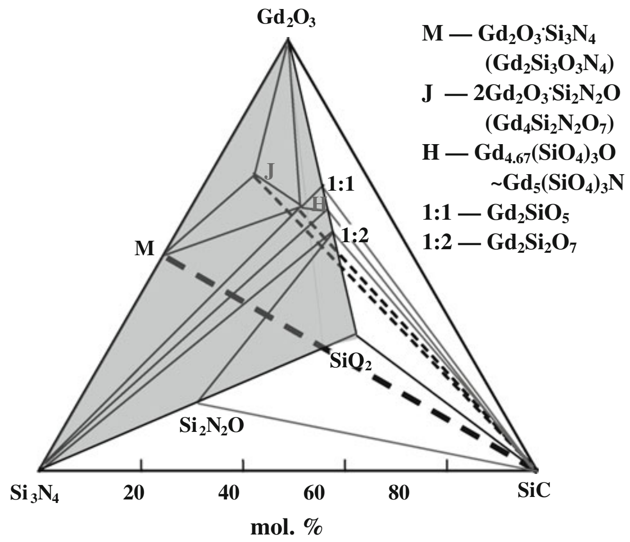

Fig. 5 Tentative phase diagram for the SiC–Si_3N_4–SiO_2–Gd_2O_3 system

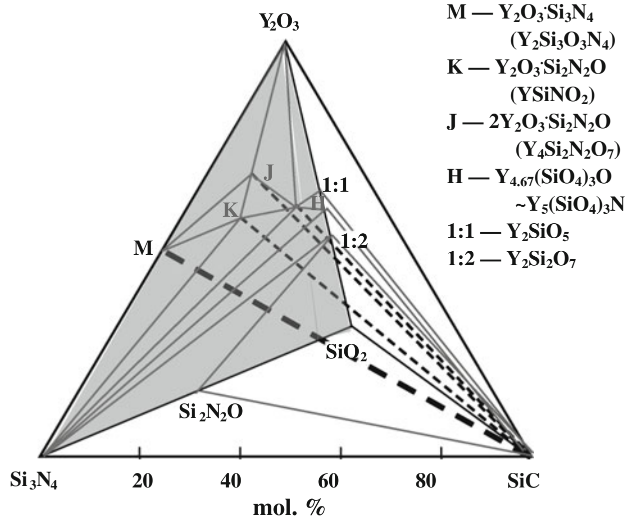

Fig. 6 Tentative phase diagram for the SiC–Si_3N_4–SiO_2–Y_2O_3 system

Y-containing systems. Combining with XRD results and the assessments of literatures data [6–12, 15], the subsolidus phase diagrams of the quaternary systems SiC–Si_3N_4–SiO_2–R_2O_3 (R = Gd and Y) can be established as Figs. 5 and 6. It is evident that the difference of two ternary Si_3N_4–SiO_2–R_2O_3 systems also reflected on that of two quaternary systems SiC–Si_3N_4–SiO_2–R_2O_3 (R = Gd and Y).

Conclusions

Subsolidus phase diagrams of the systems SiC–Si_3N_4–R_2O_3 (R = Gd and Y) have been determined. The presence of in situ SiO_2 impurity in the powder mixtures leads to form some rare-earth siliconoxynitrides and to extend the quasiternary systems into quaternary systems of SiC–Si_3N_4–SiO_2–R_2O_3, in which the subsolidus phase diagram of the system Si_3N_4–SiO_2–R_2O_3 was first time presented. A part of SiC was oxidized/nitrided by the atmosphere and then also attended to react with R_2O_3 forming some rare-earth siliconoxynitrides. They all contributed to the phase relations and constructed the subsolidus phase diagrams of the quaternary system SiC–Si_3N_4–SiO_2–R_2O_3 (R = Gd and Y). The difference of the phase relations of these two quaternary systems was indicated and discussed.

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