journal

J. Am. Ceram. Soc., 77 [10] 2763–66 (1994)

Solid–Liquid Reaction in the System Si_3N_4–$Y_3Al_5O_{12}$–$Y_2Si_2O_7$ under 1 MPa of Nitrogen

Zhen-Kun Huang and Tseng-Ying Tien*

Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan 48109

The melting behaviors of selected compositions in the system Si_3N_4–$Y_3Al_5O_{12}$–$Y_2Si_2O_7$ were determined under 1 MPa of nitrogen. The behavior phase diagrams of the ternary and their binary systems are presented. The ternary eutectic composition contains 10 wt% Si_3N_4, 27 wt% $Y_3Al_5O_{12}$, and 63 wt% $Y_2Si_2O_7$ with a eutectic temperature of 1430°C. The binary eutectic compositions and temperatures are 25 wt% Si_3N_4 and 75 wt% $Y_3Al_5O_{12}$ at 1650°C, 10 wt% Si_3N_4 and 90 wt% $Y_2Si_2O_7$ at 1570°C, and 35 wt% $Y_3Al_5O_{12}$ and 65 wt% $Y_2Si_2O_7$ at 1520°C.

I. Introduction

SILICON NITRIDE ceramics are usually densified in the presence of a reactive liquid. The liquid is normally comprised of the eutectic melt from the surface layer of the silicon nitride powder and the oxide sintering additives used. The presence of the liquid also aids the microstructural development which gives silicon nitride ceramics their superior mechanical properties.

The most common oxide sintering additives for Si_3N_4 are Y_2O_3 and Al_2O_3. Phase equilibria have been studied extensively in silicon nitride–metal oxide systems. Subsolidus phase equilibria have been reported in the systems Si,Al/N,O[1] and Si,Y/N,O.[2] The solid–liquid isotherm at 1750°C in the system Si,Al/N,O[3] has been studied. Combining the systems Si,Al/N,O and Si,Y/N,O gives the quasi-quaternary system Si,Al,Y/N,O.[4,5] The system Si,Al,Y/N,O is composed of 68 compatibility tetrahedra, but the most promising compositions for high-temperature ceramics are bounded by the Si_3N_4–Al_2O_3:AlN–YAG–$Y_2Si_2O_7$ compatibility tetrahedron.[5] YAG refers to yttrium aluminum garnet, $3Y_2O_3 \cdot 5Al_2O_3$. Si_3N_4 ceramics with YAG as a second phase have been reported by Lewis *et al.*[6] However, Hohnke and Tien[7] were the first to study the solid–liquid reactions in the Si_3N_4–β_{60}–YAG region. They found a two-phase field over the entire Si_3N_4–β_{60}–YAG plane at 1550°C, with the liquid first forming along the YAG–β_{60} join. β_{60} refers to the 60 equiv% Al–O substituted β-silicon nitride with the formula $Si_{6-x}Al_xO_xN_{8-x}$ with $x = 4$; 1650° and 1750°C isotherms in this system have also been studied by Wisnudel and Tien.[8]

The focus of this research is to clarify the solid–liquid reactions in the system Si_3N_4–YAG–$Y_2Si_2O_7$.

II. Experimental Procedure and Results

The starting powders used were Si_3N_4 (UBE-SN-E10, Japan), Al_2O_3 (AKP-50, Sumitomo Chemical Co. Ltd., Japan), Y_2O_3 (99.99%, Aldrich Chemical Co. Inc., Milwaukee, WI), and SiO_2 (Aerosil 380, Degussa Co., U.S.A.). More than 50 compositions were prepared in the system, among which the smallest interval of some compositions was 5 wt%. The starting powders of different compositions were weighed and mixed in an agate mortar and pestle under isopropyl alcohol for 1.5 h. The mixtures were dried and pressed into pellets (0.25 cm × 1 cm in diameter) and then isostatically pressed under 300 MPa. The pellets were placed on a BN powder-bed in a graphite die with a screw cap and were sintered in a graphite furnace under 1 MPa of nitrogen at different temperatures for 2 h. The natural cooling rate of the samples after sintering was 40°C/min from power-off until 1000°C. The weight loss of the samples was measured by weighing the samples before and after sintering.

X-ray diffraction was used for phase identification. Scanning electron micrographs from polished surfaces were used to quantify the amount of liquid phase present in the samples.[9] The liquid phase was crystallized after densification to verify the location of the starting composition.

Melting behaviors of some compositions were determined by visual observation. The level rule was used to determine the liquidus location. The data points collected are listed in Tables I through IV. These data were used to construct the phase diagrams in Figs. 1, 2, and 3.

III. Discussion

(1) *The Binary System Si_3N_4–$Y_3Al_5O_{12}$*

Previous reports[8] indicate that Si_3N_4 and $Y_3Al_5O_{12}$ form a binary join at 1550°C under flowing nitrogen conditions. At higher temperatures, a liquid phase is observed, and this system forms a true binary join.

In the present work on this binary system, the experimental results indicate that silicon nitride could be compatible with YAG up to a higher temperature (1630°C) under 1 MPa of nitrogen. The eutectic point in this binary system is at 1650°C with a composition of 25 wt% Si_3N_4 and 75 wt%$Y_2Al_5O_{12}$. At 1650°C the weight losses for the compositions investigated in this system were small (below 2 wt%). Figure 1 shows the behavior phase diagram of the Si_3N_4–$Y_3Al_5O_{12}$ system under 1 MPa of nitrogen. The weight loss became greater at higher temperatures. Up to 10 wt% weight loss was observed at 1800°C.

Si_3N_4-rich samples with higher weight loss showed three phases: Si_3N_4, monoclinic J_{ss}, and liquid. J_{ss} has a higher melting point (2000°C). Higher temperature and more oxygen-rich compositions favor the formation of J_{ss} phase.

(2) *The Binary System Si_3N_4–$Y_2Si_2O_7$*

The system Si_3N_4–$Y_2Si_2O_7$ is a true binary. The specimens have high weight loss. The hexagonal H-phase $Y_5(SiO_4)_3N$ often appears. The binary composition of 10 wt% Si_3N_4:90 wt% $Y_2Si_2O_7$ is the eutectic which melts at 1570°C.

(3) *The Binary System $Y_3Al_5O_{12}$–$Y_2Si_2O_7$*

The lowest melting composition in this binary system was found to contain 35 wt% $Y_3Al_5O_{12}$:65 wt% $Y_2Si_2O_7$ with a eutectic temperature at 1520°C. No weight loss was detected for

S. Danforth—contributing editor

Manuscript No. 193875. Received January 26, 1994; approved July 6, 1994.
Supported by the Ceramic Technology Project, Department of Energy Office of Transportation Technologies, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

*Member, American Ceramic Society.

Table I. Compositions, Firing Conditions, Melting Behaviors, and Crystal Phase Analyses in the System Si_3N_4–$Y_3Al_5O_{12}$ under 1 MPa of Nitrogen

	Si_3N_4:$Y_3Al_5O_{12}$ composition (wt%)	Temp (°C)	Wt loss (wt%)	Melting behaviors	Phase analyses*
(1)	100:0	1900	6.1	Not densified	α-SN, β-SN
		1800	2.1	Not densified	α-SN, β-SN
		1750	2.0	Not densified	
		1650	1.2	No melting	
(2)	80:20	1900	19.7	Large shrinkage	
		1800	5.4	Densified	SN, J_{ss}
		1750	2.0	Densified	
		1700	0.7	Densified	SN, B
		1650	0.3	Densified	SN, G, H
		1550	1.0	Not melted	SN, G
(3)	70:30	1900	15.9	Large shrinkage	SN, J_{ss}
		1800	5.9	Densified	SN, J_{ss}
		1750	3.0	Densified	SN, J_{ss}
		1700	1.0	Densified	SN, B
		1650	1.0	Densified	
(4)	60:40	1900	27.6	Large shrinkage	
		1800	6.2	Densified	SN, J_{ss}
		1750	4.1	Densified	SN, J_{ss}
		1700	2.1	Densified	SN, B, J_{ss}
		1650	0.8	Densified	
(5)	50:50	1900	16.9	Partly melted	
		1800	8.8	Partly melted	J_{ss}, SN
		1750	5.2	Partly melted	
		1700	3.7	Partly melted	J_{ss}, SN
		1650	1.8	Densified	
(6)	40:60	1800	15.5	Partly melted	
		1750	8.2	Partly melted	B, J_{ss}, SN
		1700	3.9	Partly melted	J_{ss}, SN
		1650	0.7	Partly melted	
(7)	30:70	1800	9.8	Melted (bubbles)	
		1750	4.6	Melted (bubbles)	
		1650		Partly melted	SN
		1630	1.5	No melting	
		1600	1.9	No melting	G, SN
(8)	25:75	1650	1.7	Melted (bubbles)	SN, G
		1630	0.9	No melting	
		1600	0.9	No melting	G, SN
(9)	20:80	1800	6.0	Melted (bubbles)	
		1750	2.4	Melted (bubbles)	G, J_{ss}
		1650	2.0	Mostly melted	G
		1630	2.3	Partly melted	
		1600	1.2	No melting	G, SN
		1550	1.1	No melting	G, SN
(10)	10:90	1800	3.3	Melted	
		1750	2.0	Melted (bubbles)	
		1650		Slightly melted	

*SN = Si_3N_4 (α and/or β), G = $Y_3Al_5O_{12}$ (YAG or garnet), B = Y_2SiAlO_5N (B-phase), J_{ss} = solid solution of $2Y_2O_3{\cdot}Si_2N_2O$ and $2Y_2O_3{\cdot}Al_2O_3$, H = $Y_5(SiO_4)_3N$ (H-phase).

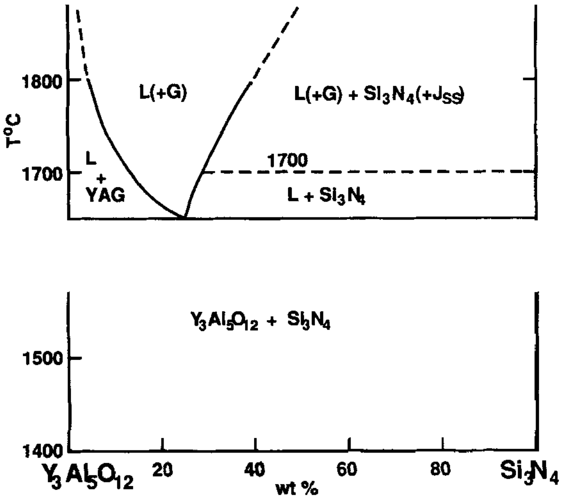
Table II. Compositions, Firing Conditions, Melting Behaviors, and Crystal Phase Analyses in the System Si_3N_4–$Y_2Si_2O_7$

	Si_3N_4:$Y_2Si_2O_7$ composition (wt%)	Temp (°C)	Wt loss (wt%)	Melting behaviors	Phase analyses*
(11)	80:20	1650	4.7	Densified	
		1550	2.0	Not melted	SN, H
(12)	70:30	1650	6.8	Densified	SN, H
(13)	60:40	1650	4.1	Densified	SN, H
(14)	50:50	1650	5.1	Densified	H, SN
(15)	40:60	1650	6.4	Slightly melted	H, SN, YS
(16)	30:70	1650		Melted (bubbles)	YS, H, SN
		1550	3.4	No melting	
		1500	2.2	No melting	
(17)	20:80	1650	12.0	Melted	YS, SN, H
		1550		No melting	
(18)	15:85	1600	3.4	Melted (bubbles)	
(19)	10:90	1650	9.3	Melted	
		1600	4.1	Melted (bubbles)	
		1550	1.2	No melting	YS, SN
(20)	05:95	1650	4.8	Melted	
		1630	6.7	Slightly melted	

*SN = Si_3N_4 (α and/or β), H = $Y_5(SiO_4)_3N$ (H-phase), YS = $Y_2Si_2O_7$.

Table III. Compositions, Firing Conditions, Melting Behaviors, and Crystal Phase Analyses in the System YAG–$Y_2Si_2O_7$

(21)	50:50	1650	1.7	Melted	
		1600	0.0	Melted (bubbles)	
		1550	0.3	Melted	
		1530	0.4	Slightly melted	
(22)	40:60	1650	0.7	Melted	
		1600	0.0	Melted	
		1550	0.3	Melted	
		1530	1.0	Melted	
		1500	0.9	No melting	G, YS
(23)	30:70	1650	2.5	Melted	
		1600	0.0	Melted	
		1550	0.3	Melted	
		1530	0.4	Melted	
		1500	0.3	No melting	YS, G



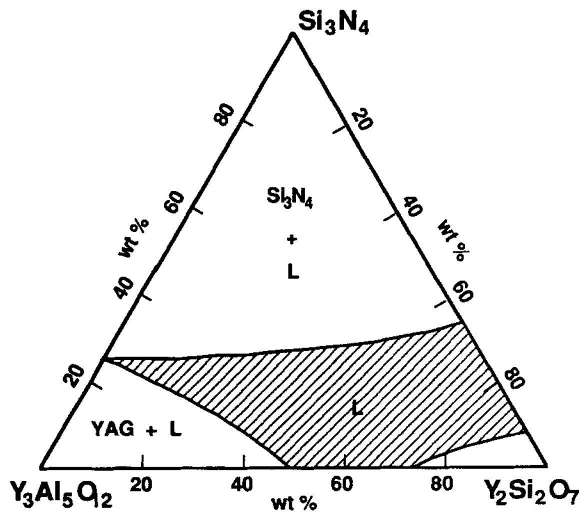


Fig. 3. The system Si_3N_4–$Y_2Si_2O_7$–$Y_3Al_5O_{12}$ at 1650°C.

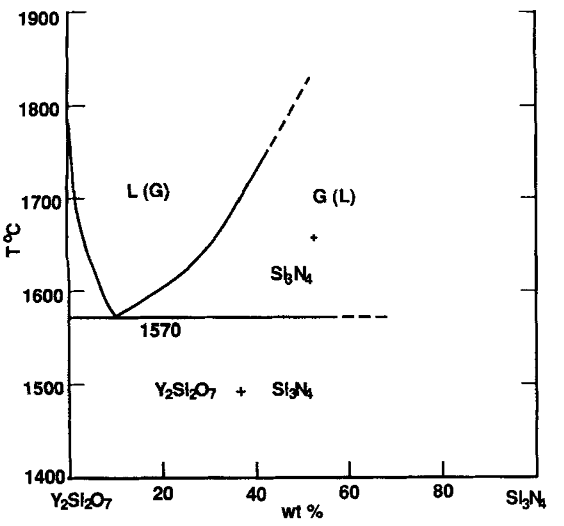


Fig. 2. The system Si_3N_4–$Y_2Si_2O_7$.

Figure 3 shows the 1650°C isothermal section of this ternary system. An extended liquid area near the oxide side (far from Si_3N_4) was observed. The lowest melting composition contained 10 wt% Si_3N_4, 27 wt% $Y_3Al_5O_{12}$, and 63 wt% $Y_2Si_2O_7$ with a ternary eutectic temperature at 1430°C.

Higher weight losses were observed at 1650°C. Melted samples with compositions within the liquid area often contained bubbles. A translucent nitrogen-containing glass without bubbles could be obtained only for the compositions containing <12 at.% or <6 wt% nitrogen, compositions surrounding the lowest melting point.

IV. Summary

The melting behaviors in the system Si_3N_4–$Y_3Al_5O_{12}$–$Y_2Si_2O_7$ were determined under 1 MPa of nitrogen. The behavior phase diagrams of the ternary and their binaries have been presented. The ternary eutectic composition contains 10 wt% Si_3N_4, 27 wt% $Y_3Al_5O_{12}$, and 63 wt% $Y_2Si_2O_7$ with a eutectic temperature of 1430°C.

The binary eutectic compositions and temperatures are 25 wt% Si_3N_4 and 75 wt% $Y_3Al_5O_{12}$ at 1650°C, 10 wt% Si_3N_4 and 90 wt% $Y_2Si_2O_7$ at 1570°C, and 35 wt% $Y_3Al_5O_{12}$ and 65 wt% $Y_2Si_2O_7$ at 1520°C.

Table IV. Compositions, Firing Conditions, Melting Behaviors, and Crystal Phase Analyses in the System Si_3N_4–YAG–$Y_2Si_2O_7$

	Si_3N_4:YAG:$Y_2Si_2O_7$ composition (wt%)	Temp (°C)	Wt loss (wt%)	Melting behaviors	Phase analyses*
(24)	80:15:5	1650	0.4	Densified	SN, G, YS, H
(25)	80:10:10	1650	1.0	Densified	SN, YS, H
		1550	0.6	No melting	
(26)	80:5:15	1650	1.2	Densified	SN, YS
		1550	0.9	No melting	
(27)	50:40:10	1650	1.9	Partly melted	
(28)	50:30:20	1650	2.5	Partly melted	
(29)	50:20:30	1650	3.0	Partly melted	
(30)	50:10:40	1650	3.9	Partly melted	
(31)	40:48:12	1650	1.8	Mostly melted	
(32)	40:36:24	1650	1.8	Mostly melted	
(33)	40:24:36	1650	2.5	Mostly melted	
(34)	40:12:48	1650	3.1	Mostly melted	
(35)	35:45.5:19.5	1650	2.6	Melted	
(36)	35:32.5:32.5	1650	2.5	Melted	
		1550	0.8	Mostly melted	
(37)	35:19.5:45.5	1650	5.0	Melted	
		1550	0.8	Mostly melted	
(38)	30:56:14	1650		Mostly melted	
		1550	1.8	No melting	
(39)	30:42:28	1650		Melted (bubbles)	
		1550	2.1	Mostly melted	
(40)	30:28:42	1650		Melted (bubbles)	
		1550	2.3	Melted	
		1500	1.3	Partly melted	
(41)	30:14:56	1650		Melted (bubbles)	
		1550	1.3	Melted	
		1500	1.5	Partly melted	
(42)	20:72:8	1650	3.7	Melted (bubbles)	
		1600	0.6	No melting	G, SN, H
(43)	20:64:16	1650	3.0	Melted (bubbles)	
		1550	0.6	Little melted	
(44)	20:48:32	1650	4.8	Mostly melted	
		1550	1.1	Partly melted	
(45)	20:32:48	1650	3.4	Melted (bubbles)	
		1550	0.6	Melted	
		1500	0.6	Mostly melted	
		1450	0.4	Mostly melted	
(46)	20:16:64	1650	6.2	Melted (bubbles)	
		1550	1.2	Mostly melted	
		1500	0.4	Mostly melted	
		1450	0.1	No melting	H, SN
(47)	15:42.5:42.5	1550	0.6	Melted	
		1430	0.6	No melting	
(48)	15:25.5:59.5	1550	2.5	Melted	
		1450	0.5	Melted	
		1430	1.2	Mostly melted	
(49)	15:8.5:76.5	1650	9.6	Melted (bubbles)	
(50)	10:72:18	1650	3.3	Melted (bubbles)	
		1550	1.4	Partly melted	
(51)	10:54:36	1550	1.6	Mostly melted	
(52)	10:36:54	1550	1.5	Melted	
		1500	1.4	Melted	
		1450	0.4	Melted	
		1430	0.1	Little melted	
(53)	10:27:63	1430	1.5	Melted (T_{eu})	
(54)	10:18:72	1550	0.8	Melted	
		1500	1.6	Melted	
		1450	0.3	Mostly melted	
		1430	1.0	Slightly melted	
(55)	5:28.5:66.5	1430		Mostly melted	

*SN = Si_3N_4 (α and/or β), G = $Y_3Al_5O_{12}$ (YAG or garnet), H = $Y_5(SiO_4)_3N$ (H-phase), YS = $Y_2Si_2O_7$.

References

[1] L. J. Gauckler, H. L. Lukas, and G. Petzow, "Contribution to the Phase Diagram Si_3N_4–AlN–Al_2O_3–SiO_2," *J. Am. Ceram. Soc.*, **58** [7–8] 346–47 (1975).

[2] L. J. Gauckler, H. Hohnke, and T.-Y. Tien, "The System Si_3N_4–SiO_2–Y_2O_3," *J. Am. Ceram. Soc.*, **63** [1–2] 35–37 (1980).

[3] I. K. Naik and T.-Y. Tien, "Subsolidus Phase Relations in Part of the System Si,Al,Y/N,O," *J. Am. Ceram. Soc.*, **62** [11–12] 642–43 (1979).

[4] I. K. Naik, L. J. Gauckler, and T.-Y. Tien, "Solid–Liquid Equilibrium in the System Si_3N_4–AlN–SiO_2–Al_2O_3," *J. Am. Ceram. Soc.*, **61** [7–8] 332–35 (1978).

[5] W.-Y. Sun, T.-Y. Tien, and T.-S. Yen, "Subsolidus Phase Relationships in Part of the System Si,Al,Y/N,O: The System Si_3N_4–AlN–YN–Al_2O_3–Y_2O_3," *J. Am. Ceram. Soc.*, **74** [11] 2753–58 (1991).

[6] M. H. Lewis, A. R. Bhatti, R. J. Lumby, and B. North, "The Microstructure of Sintered Si-Al-O-N Ceramics," *J. Mater. Sci.*, **15** [1] 103 (1980).

[7] H. Hohnke and T.-Y. Tien, "Solid–Liquid Reaction in Part of the System Si,Y/N,O"; pp. 101–10 in *Progress in Nitrogen Ceramics*. Edited by F. L. Riley. Martinus Nijhoff, Boston, MA, 1983.

[8] M. Wisnudel and T.-Y. Tien, "Solid–Liquid Reactions in the System Si_3N_4–β-SiAlON–YAG," *J. Am. Ceram. Soc.*, in press.

[9] E. Underwood, *Quantitative Stereology*. Addison-Wesley, Reading, MA, 1970.