Reaction Densification of α' -SiAlON: I, Wetting Behavior and Acid–Base Reactions

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Phase development during reaction hot pressing of α -Si₃N₄, AlN, Al₂O₃, and M₂O₃ powder mixtures (M = Li, Mg, Ca, Y, Nd, Sm, Gd, Dy, Er, and Yb) forming α' -SiAlON has been studied. The wetting behavior of the ternary eutectic melt of M₂O₃–Al₂O₃–SiO₂ was found to control the reaction sequence during hot pressing. Li, Ca, Mg, Nd, Sm, and Gd were found to preferentially wet and react with Si₃N₄ first, whereas Dy, Er, and Yb preferentially wetted and reacted with AlN first. The intermediate phases are Si rich in the former and Al rich in the latter case. Pearson's principle of acid–base theory, which predicts decreasing basicity of oxides of Li, Ca, Mg, Nd, Gd, Sm, Dy, Er, and Yb and decreasing acidity of oxides of Si and Al, is used to understand these reactions.

I. Introduction

REACTION hot pressing of Si₃N₄ is a well-established technique for the fabrication of dense SiAlON ceramic. A typical batch consists of a mixture of Si₃N₄, AlN, Al₂O₃, and a metal oxide. Commonly used metal oxides are Li₂O, MgO, CaO, or Y₂O₃.^{1–4} The process begins with the native SiO₂ present on the Si₃N₄ particles reacting with the oxide additives to form a eutectic melt. This liquid facilitates the densification and the subsequent phase transformations through a solution–reprecipitation mechanism.^{1,2,5,6} The characteristics of the eutectic melt, which may preferentially wet either Si₃N₄ or AlN, play an important role in determining the reaction pathway and densification behavior.

A survey of the literature indicates that there is almost no knowledge of the wetting characteristics of various ternary oxide eutectic melts on nitrides. Most studies on reaction sintering have been restricted to the documenting of phase evolution and densities. Some information can be gleaned from the reports of transient/intermediate phases of these studies. Sun *et al.*⁷ and Slasor and Thompson⁸ have studied reaction sequences in Ca-, Y- and Nd- α' -SiAlON. Gehlenite (Ca₂Al₂SiO₇) was found to be the transient phase in Ca- α' -SiAlON, whereas N-melilite (R₂Si₃O₃N₄) formed during the densification of Y- and Nd- α' -SiAlON. Hampshire *et al.*⁹ found N-melilite to be the transient phase in Nd- and Sm-doped α' -SiAlON. O'Reilly *et al.*¹⁰ also found N-melilite as a transient phase in their study of pressureless sintering of lanthanide (Y and from Nd to Lu except Pm)-modified α' -SiAlON. K (RSiO₂N) and β -Si₃N₄ phase along with melilite was found by Wang *et al.* in the case of Nd- α' -SiAlON.¹¹ Furthermore, they found J (R₄Si₂O₂N) and β -Si₃N₄ phase in the case of Sm- and Gd- α' -SiAlON along with melilite, J and β -Si₃N₄ phase in case of Dy-, Y-, Er- and Yb- α' -SiAlON. Kuang *et al.* found O'-SiAlON as a transient phase in the Li system.¹² The reaction

sequences in hot-isostatic-pressed and pressureless-sintered, rare-earth-doped α' - + β' -SiAlON have been studied by Ekstrom and co-workers.^{13–17} They reported formation of 12H and La-silicon-oxynitride as the transient phase in the case of Y- or Y/La-doped samples. Generally, it is not known what controls the formation and selection of the various phases.

Recently Hwang and Chen reported that, in the Y-SiAlON system, Y₂O₃–Al₂O₃–SiO₂ melt preferentially wets AlN, leading to the formation of β_{60} -SiAlON as the transient phase. Furthermore, the preferential wetting of AlN was found to delay the densification in the early stages due to liquid trapping.⁶ These findings offer hope that a general understanding of reaction sequences in these complicated systems may, after all, be based on simple physical chemical considerations governing surface activities of nitrides with reactive liquids.

Motivated by the above study, we report the reaction sequences during hot pressing of M- α' -SiAlON (M = Li, Ca, Mg, Nd, Sm, Gd, Dy, Er, and Yb). The wetting properties of M₂O₃–Al₂O₃–SiO₂ ternary oxide melts are also studied. Using simple thermodynamic calculations and concepts in acid–base chemistry, we are able to relate the systematic difference in the wetting reactions and transient phase formation to the acidity/basicity of different oxide melts and nitride particles. In the second part of this series we present the densification results and discuss the effect of wetting behavior thereon.¹⁸

II. Experimental Procedure

(1) Composition

The compositions investigated lie on the so-called α' -plane represented by the formula M_pSi_{12-(m+n)}Al_(m+n)O_nN_(16-n). Specifically, $m = 1.0$, $n = 1.0$ (1010) and $m = 1.2$ and $n = 1.0$ (1210) are chosen because they lie inside the single-phase α' region (Fig. 1). These compositions, given in weight percent of starting powders, are also shown in Table I of part II¹⁸ for later reference. Oxides studied here are known to enter α' -SiAlON as a solid-solution additive. Lattice parameters increase upon alloying, because the metal cations occupy the interstitial sites in the parent Si₃N₄ structure.

(2) Powder Preparation

The compositions were prepared in 43 g batches from the starting powders (α -Si₃N₄, UBE, E10; AlN, Tokuyama Soda, Type F; Al₂O₃, Sumitomo Chemical America, AKP50; Li₂O, Aldrich Chemical; CaO, Matheson Coleman Bell Manufacturing Chemists; MgO, Biakowski International; Y₂O₃, Aldrich Chemical; Nd₂O₃, Sm₂O₃, Dy₂O₃, Y₂O₃, Er₂O₃, and Yb₂O₃, Alfa Johnson Matthey). The powders were attrition milled in 2-propanol in a Teflon-coated jar using high-purity alumina balls. Native oxides on the nitride powders and alumina pickup from the milling step were compensated for in the formulation of the batch. After milling, the powder slurry was dried under stirring in a Teflon beaker at 80°C.

(3) Hot Pressing

Charges of 14 g powders were hot pressed in a graphite resistance furnace under 1 atm nitrogen. The compact was first

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Fig. 1. α' plane in a Janecke prism showing compositions studied. The delineated phase boundary varies with metal oxide additives.

cold pressed at 27 MPa. The heating rate up to 1000°C was 25°C/min and then 15°C/min to the hold temperature. A load of 27 MPa was applied during heating, holding, and cooling whenever the temperature exceeded 1000°C. The shrinkage of the powder compacts, as represented by the ram movement, was monitored by an LVDT with an accuracy of 0.1 mm. The expansion of the load train was subtracted from the travel data. All the compositions were hot pressed to 1750°C and, when no movement was detected for 5 min at this temperature, the furnace was shut down and the specimen allowed to cool. Separate runs were also repeated but interrupted at temperatures below 1750°C to study the phase evolution. Hot pressing was repeated for all the compositions from which the data reproducibility was verified.

(4) Wetting Experiments

The purpose of the wetting experiments is to study the trends in the wetting behavior of the ternary oxide melt on the nitrides. To accomplish this goal, the following wetting experiment was designed. Ternary eutectic compositions of SiO_2 (U.S. Silica), Al_2O_3 , and a M_2O_3 (Li_2O , MgO , Sm_2O_3 and Yb_2O_3) were prepared and pressed into a pellet. Si_3N_4 and AlN were hot pressed without any additive at 1750°C (not fully dense) for substrates. The pellets were then placed on the substrates and heated to different temperatures, in a nitrogen atmosphere, where the pellets fused. They were held there for 12 min and cooled to room temperature. The contact angles were measured from photomicrographs of cooled specimens. It should be noted that the wetting characteristics are sensitive to the composition (including the oxygen/nitrogen content in the melt) and the temperature; hence, it underwent changes during our experiments, and true equilibrium was probably not attained. Thus, these experiments do not yield the actual value of the wetting angle. Rather it provides an insight into the preferential wetting of the nitride powder by the ternary oxide melt in a multicomponent system.

(5) Characterization

The reaction products were identified by X-ray diffraction (XRD) techniques. Si was used as the internal standard for the calculation of the lattice parameters. α' -SiAlON was identified by the deviation of the lattice parameters (see Table I) from that of α - Si_3N_4 . JCPDS Cards used for identification were No.

Table I. Lattice Parameters for α' -SiAlON

Composition	Temp. (°C)	<i>a</i> (Å)	<i>c</i> (Å)
Li 1010	1300	7.7543	5.6301
Li 1010	1420	7.7620	5.6401
Li 1010	1750	7.8233	5.6855
Ca 1010	1550	7.7843	5.6172
Ca 1010	1750	7.8115	5.6375
Mg 1010	1570	7.7726	5.6406
Mg 1010	1750	7.8225	5.6370
Mg 1010	1850	7.8228	5.6489
Nd 1210	1575	7.7527	5.6308
Nd 1210	1750	7.8403	5.7324
Sm 1210	1420	7.7575	5.6311
Sm 1210	1575	7.8049	5.6335
Sm 1210	1750	7.8189	5.6364
Gd 1210	1675	7.8276	5.5733
Gd 1210	1750	7.8701	5.6286
Dy 1210	1575	7.8146	5.6446
Dy 1210	1675	7.8164	5.6983
Dy 1210	1750	7.8480	5.6692
Er 1210	1475	7.7549	5.6248
Er 1210	1750	7.8178	5.7205
Yb 1210	1575	7.7499	5.5922
Yb 1210	1750	7.8231	5.6355

41-360 for α - Si_3N_4 , Card No. 33-1162 for α' -SiAlON, Card No. 31-884 for Nd melilite, Card No. 31-1216 for Sm melilite, Card No. 32-12 for the Er-garnet ($\text{Er}_3\text{Al}_5\text{O}_{12}$), Card No. 23-1476 for Yb-garnet ($\text{Yb}_3\text{Al}_5\text{O}_{12}$), and Card No. 14-249 for the magnesium-aluminosilicate phase. Lattice parameters for β' were refined with a least-squares fit, and x in the formula ($\text{Si}_{6-x}\text{Al}_x\text{O}_{8-x}\text{N}_{2+x}$) was calculated using the calibration curve developed by Ekstrom *et al.*¹⁴ For melilite solid solution ($\text{R}_2\text{Si}_3\text{Al}_x\text{O}_{3+x}\text{N}_{4-x}$), the lattice parameters were fitted to

$$a = 4.8735 + 2.58r + 0.049x$$

where a is the cell dimension of the tetragonal cell, and r is the radius of the rare-earth ion, both in Angstroms. Their dependence was determined from N-melilite $\text{R}_2\text{Si}_3\text{O}_3\text{N}_4$ with $\text{R} = \text{Y}$, Sm , and Nd , whereas x dependence is assumed to be the same as that given by Cheng and Thompson¹⁹ for Sm-melilite solid solution.

III. Results

(1) Alkali and Alkaline-Earth Oxides

The systems studied here were M-1010, with M being Li, Ca, and Mg.

(A) *Li System:* XRD patterns of samples hot pressed to intermediate temperatures (1300°, 1420°, and 1550°C) revealed the following (Fig. 2). First, all the oxide peaks have disappeared above 1300°C, indicating complete melting. Second, α' -SiAlON ($\text{Si}_2\text{N}_2\text{O}$) was formed above 1300°C. Third, unreacted AlN was still present below 1550°C. Fourth, α' started disappearing above 1550°C. Fifth, a single-phase α' -SiAlON was formed at 1750°C. Sixth, α' started forming at 1420°C (Table I).

The dependence of wetting angle on temperature for Li_2O - Al_2O_3 - SiO_2 eutectic ($\text{Li}_2\text{O} = 19$ wt%, $\text{SiO}_2 = 68$ wt%, $\text{Al}_2\text{O}_3 = 13$ wt%)²⁰ on Si_3N_4 and AlN is shown in Fig. 3. These curves indicate that the melt wets Si_3N_4 preferentially. The actual wetting is probably between 1200° and 1300°C, since by 1350°C all the melt had reacted with the Si_3N_4 substrate. The reaction layer (at 1350°C) on the substrate was found to contain α' -SiAlON according to the XRD pattern.

Fig. 2. XRD pattern of Li-1010 samples showing the phase evolution.

(B) *Ca System:* XRD studies of samples hot pressed to intermediate temperatures (1550° and 1650°C) revealed the following. First, there were no oxide peaks present at 1550°C. Second, O' was formed at 1550°C. Third, a small amount of unreacted AlN was also found at the same temperature. Fourth, O' started to disappear at 1650°C. Fifth, a single-phase α' -SiAlON at 1750°C was formed. Sixth, α' started to form at 1550°C (Table I). The above reaction sequence of phase evolution is similar to that of Li-1010, and the XRD patterns are thus not shown here.

Wetting experiments indicate that the ternary eutectic (CaO = 50.1 wt%, Al_2O_3 = 43.5 wt%, SiO_2 = 6.4 wt%)²⁰ preferentially wets and reacts with Si_3N_4 (Fig. 3). Wetting was complete at 1500°C. The above sequence also parallels that of Li-1010.

(C) *Mg System:* XRD studies of samples hot pressed to 1570°, 1750°, and 1850°C revealed the following (Fig. 4). First, there were no oxides present at 1570°C, indicating complete melting. Second, a small amount of unreacted AlN was found at 1570°C. Third, a magnesium-aluminosilicate phase, $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, called μ -cordierite, was found above 1570°C. Fourth, some α' , $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, and AlN were detected at 1850°C. The sample was not fully dense at this temperature after 30 min. Fifth, formation of α' started around 1570°C (Table I).

Wetting experiments show that the ternary eutectic (MgO = 25.3 wt%, Al_2O_3 = 19.4 wt%, SiO_2 = 55.3 wt%)²⁰ has a lower

Fig. 4. XRD pattern of Mg-1010 samples showing the phase evolution.

wetting angle on AlN (Fig. 5). However, XRD analysis revealed a reaction product (Fig. 6), $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ on the Si_3N_4 substrate, at 1500°C; no reaction product formed on the AlN substrate.

The above results indicate that the Mg-containing compact, Mg-1010, follows a reaction sequence different than that from Li- and Ca-1010.

(2) Rare Earths

The rare earths studied were R-1210, where R is the even-number rare-earth elements, Nd, Sm, Gd, Dy, Er, and Yb. The transient phase formed in the case of Nd, Sm, and Gd was found to be a melilite solid solution, whereas that in the case of Er and Yb was a garnet phase and β' -SiAlON. Based on this, the rare-earth system is further classified into two groups, plus the intermediate cases.

(A) *Lighter Rare Earths (Nd, Sm):* XRD studies of samples hot pressed to 1420°, 1575°, 1750°C (Fig. 7) revealed the following. First, all the oxide peaks were absent at 1420°C, suggesting complete melting. Second, melilite solid solution ($\text{R}_2\text{Si}_3\text{Al}_x\text{O}_{3+x}\text{N}_{4-x}$) started to form at 1420°C. The melilite solid solution (M') was found to be supersaturated in Al_2O_3 ($x = 1.0$). Third, unreacted AlN was found at 1575°C. Fourth, both α' -SiAlON and M' were found at 1750°C. Fifth, formation of α' started at 1420°C (Table I).

Fig. 3. Variation of wetting angle with temperature for Li_2O - SiO_2 - Al_2O_3 eutectic melt and Si_3N_4 /AlN.

Fig. 5. Variation of wetting angle with temperature for MgO - SiO_2 - Al_2O_3 eutectic melt on Si_3N_4 /AlN.

- α - Si_3N_4
- α' - SiAlON
- * $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$

Fig. 6. XRD pattern of reaction layer between $\text{MgO-SiO}_2\text{-Al}_2\text{O}_3$ ternary melt and Si_3N_4 .

Wetting experiments using ternary oxide ($\text{Sm}_2\text{O}_3 = 30$ mol%, $\text{Al}_2\text{O}_3 = 20$ mol%, $\text{SiO}_2 = 50$ mol%)²¹ indicate that the liquid preferentially wets Si_3N_4 and complete wetting is achieved at 1550°C (Fig. 8). The reaction at 1450°C resulted in the formation of M' on the substrate.

(B) *Heavier Rare Earths (Er, Yb):* XRD of the samples hot pressed to 1475° , 1575° , 1675° , and 1750°C revealed the following (Fig. 9). First, all oxides were absent at 1475°C , indicating complete melting. Second, a garnet phase, $\text{R}_3\text{Al}_5\text{O}_{12}$ was formed at 1475°C . Third, at 1575°C , this phase disappeared and β' - SiAlON was formed along with α' - SiAlON . Fourth, at 1750°C single-phase α' was found. Fifth, formation of α' started at 1575°C (Table I). The β' formed was found to be β_{60} ($x = 4.2$, in $\text{Si}_{6-x}\text{Al}_x\text{O}_{8-x}$). These results are similar to those in the case of the Y-SiAlON system, reported by Hwang and Chen,⁶ where a single-phase β_{60} was found at 1650°C . The β' - SiAlON later disappeared and α' - SiAlON was formed at higher temperatures.

- # AlN
- α - Si_3N_4
- * Melilite
- α' - SiAlON

Fig. 7. XRD pattern of Sm-1210 samples showing the phase evolution.

Fig. 8. Variation of wetting angle with temperature for $\text{Sm}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ eutectic melt on $\text{Si}_3\text{N}_4/\text{AlN}$.

Wetting experiments show that the ternary oxide ($\text{Yb}_2\text{O}_3 = 15$ mol%, $\text{Al}_2\text{O}_3 = 30$ mol%, $\text{SiO}_2 = 55$ mol%)²² wets AlN first (Fig. 10). This already occurs at 1450°C and is complete at 1550°C . The reaction layer on the AlN substrate was also examined and β' - SiAlON and $\text{Yb}_3\text{Al}_5\text{O}_{12}$ phases were found (Fig. 11). This is again similar to that of the Y-containing system, where $\text{Y}_3\text{Al}_5\text{O}_{12}$ and β_{60} - SiAlON were observed by Hwang and Chen.⁶

(C) *Intermediate Rare Earths (Gd, Dy):* XRD on the Gd samples hot pressed at 1575° , 1675° , and 1750°C revealed the following (Fig. 12). First, M' started to form at 1575°C . Second, unreacted AlN was found at 1575°C . Third, single-phase α' - SiAlON was found at 1750°C . Fourth, α' - SiAlON was present at 1575°C . It is apparent that Gd is similar to lighter rare earths except that single-phase α' - SiAlON , without M' , was formed at 1750°C .

XRD on the Dy samples hot pressed at 1750°C revealed that the phase evolution in the case of Dy was similar to that of heavier rare earths except that the α' reflections in Dy-1210 obtained at 1750°C had different relative intensities for (200) reflection from those of other samples (Fig. 13(a)). Annealing at 1800°C for 2 h restored the standard pattern (Fig. 13(b)), indicating that the α' - SiAlON in Dy-1210 initially has a slightly different structure. Also, as shown in the accompanying paper, single-phase α' - SiAlON is formed at 1575°C after 35 min.

A summary of results is given in Table II for later reference. Readers should also refer to Table III of part II¹⁸ for phase assemblage obtained after hot pressing at lower temperatures.

Fig. 9. Variation of wetting angle with temperature for $\text{Yb}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ ternary melt on $\text{Si}_3\text{N}_4/\text{AlN}$.

Fig. 10. XRD pattern of reaction layer between $\text{Yb}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ ternary melt and AlN.

Fig. 11. XRD pattern of Er-1210 showing the phase evolution.

Table II. Summary of Wetting Behavior and Reaction Products

Classification of additives	Additive	Phase(s) after oxide melting	First nitride wetted/intermediate phase	Final phase (at 1750°C)
Li and Ca	Li	Eutectic* + liquid	$\text{Si}_3\text{N}_4/\text{O}'$	α'
	Ca	Eutectic* + liquid	$\text{Si}_3\text{N}_4/\text{O}'$	α'
Mg	Mg	Eutectic* + liquid	$\text{Si}_3\text{N}_4/\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	$\alpha' + \text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$
Lighter rare earth	Nd	Eutectic* + liquid	$\text{Si}_3\text{N}_4/\text{M}'$	$\alpha' + \text{M}'$
	Sm	Eutectic* + liquid	$\text{Si}_3\text{N}_4/\text{M}'$	$\alpha' + \text{M}'$
Intermediate rare earth	Gd	Eutectic* + liquid	$\text{Si}_3\text{N}_4/\text{M}'$	α'
	Dy	Eutectic* + $3\text{Dy}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$	AlN/β_{60}	α'
Heavier rare earth	Er	Eutectic* + $3\text{Er}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$	AlN/β_{60}	α'
	Yb	Eutectic* + $3\text{Yb}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$	AlN/β_{60}	α'

* $\text{M}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ ternary eutectic. $\text{O}' = \text{Si}_3\text{N}_2\text{O}$. $\text{M}' = \text{R}_2\text{Si}_{3-x}\text{AlO}_{3+x}\text{N}_{4-x}$ ($x = 1$). $\beta_{60} = \text{Si}_{1.8}\text{Al}_{4.2}\text{O}_{4.2}\text{N}_{3.8}$.

Table III. Oxides in Decreasing Basicity

Additive	Field strength, z/r^* (nm^{-1})	IP ³³ of Metal ion [†] (MJ/mol)	pH ₀
Li_2O	3.01	0.5203	11.76
CaO	5.51	1.7352	10.67
MgO	6.06	2.1884	10.27
Nd_2O_3	8.25	3.694	8.93
Gd_2O_3	8.38 [‡]	3.752 [‡]	8.88
Y_2O_3	8.49	3.777	8.86
Sm_2O_3	8.32	3.871	8.77
Dy_2O_3	8.45	3.898	8.75
Er_2O_3	8.52	3.930	8.72
Yb_2O_3	8.58	4.1934	8.49
Al_2O_3	9.52	5.140	7.64
SiO_2	13.07	9.950	3.36

* $r = 2r_0 + r_{++}$. [†]IP is the total ionization energy for first z th electrons, [‡]larger due to half-filled f orbital.

Fig. 12. XRD pattern of Gd-1210 samples showing the phase evolution.

IV. Discussion

(1) Reaction Pathways in the M-Si-Al-O-N System

There appears to be a systematic correlation between the wetting behavior and the intermediate phase formed. In all cases, the intermediate phase in the compact is also the one formed on the nitride substrate that is preferentially wetted. The systems which prefer wetting of Si_3N_4 form intermediate phases

(2) The preference in the reactions between various ternary oxide melts and the nitride powders is rationalized by Pearson's principle of acid–base reactions. Hard acid, Si_3N_4 , reacts with hard bases of oxide melts of Li, Ca, Mg, and lighter rare-earth metals up to Gd, whereas the soft acid AlN reacts with the soft bases of the heavier rare-earth metals down to Dy. Native oxides on the nitride surfaces are thought to control their acidity and reactivity.

(3) The Si/Al ratio of the intermediate compounds formed during reaction densification of α' -SiAlON correlates well with the basicity of the additive oxides. In the order of decreasing Si/Al ratio and additive basicity, typical intermediate phases are O' (SiN_2O_2), μ -cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), M' ($\text{R}_2\text{Si}_2\text{AlO}_4\text{N}_3$), and β_{60} -SiAlON ($\text{Si}_{1.8}\text{Al}_{4.2}\text{O}_{4.2}\text{N}_{3.8}$).

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