Enhancing materials design capability through understanding multicomponent phase relationships

Dong-Sheng Yan

State Key Laboratory on High Performance Ceramics and Superfine Microstructure,
Shanghai Institute of Ceramics, Chinese Academy of Sciences
1295 Dingxi Road
Shanghai 200050, China

Abstract: Most advanced ceramic materials are complex in their phase compositions which in turn influence their microstructure and properties. The study of the phase relationships of multicomponent systems will provide useful information concerning compatibility of phase assemblages based on thermodynamic principles. Such knowledge will serve as a powerful tool for the materials scientists to design materials with relevant phases that may perform with desirable and better properties. Advanced nitride materials have been chosen in this paper to illustrate this approach of enhancing materials design capability with some case study examples.

I. INTRODUCTION

Most advanced ceramic materials are complex in composition and are usually multiphased in their microstructure. It appears, therefore attractive and important to be able to design their composition thus to achieve desired phase assemblages leading to optimized properties and performance. To realize such purposes, the understanding of phase relationships of multicomponent systems based on thermodynamic principles is relevant. In this talk, the enhancement of materials design capability through such an approach will be addressed by choosing advanced nitride materials as examples of case study.

Silicon nitride ceramics is a family of materials that has received increasingly keen interest for high performance engineering applications due to the fact that they generally possess high mechanical properties, superb wear resistance, good anti-oxidation and thermal shock behavior up to high temperatures. From structural chemistry point of view, this materials family is constituted with $[SiN_4]$ and $[(Si,Al)(N,O)_4]$ as the basic building units. Since the nature of the Si-N bond is highly covalent, thus renders the coefficients of diffusivity of both Si and N being very low even at high temperatures. The consequence of which is that additives, usually metal oxides, are necessary to achieve densification through liquid phase sintering. Metal oxides form a liquid phase at and beyond the eutectic temperatures. Densification is carried out through a solution -- diffusion -- precipitation processes. After the completion of sintering, the liquid phase will be cooled down to an intergranular glassy phase or partially crystallized into crystalline phases depending on the compositions, rate of cooling and subsequent heat-treatment conditions. Therefore, what one will be facing are various M-Si-Al-O-N multicomponent systems which have decisive bearings on the appearance of the major crystalline phases, the grain boundary phases as well as their microstructure. The significance of phase relationship studies of such complex Si-Al-O-N (Sialon) systems is, thus, to provide information for: (a) the selection of effective sintering aids; (b) the design of nitride ceramics with a single or composite major crystalline phases; and (c) the tailoring of grain boundary phases.

II. PHASE RELATIONSHIPS IN THE COMPLEX M-Si-Al-O-N SYSTEMS

II.1 Fundamentals about silicon nitride

Si_3N_4 has two different crystalline polymorphs, namely α-Si_3N_4 and β-Si_3N_4.[1-4] The structural difference between them is the result of different ways of stacking the Si-N layers as shown in Fig. 1. The β-Si_3N_4 structure is obtained by ABAB ... stacking with space group P63/m. This structure leads to continuous channels parallel to the C-direction. While the α-Si_3N_4 structure is the result of an ABCD stacking with a space group P3/c. The channels are thus closed and as a result, there are 2 large interstitial sites in each unit cell, where cations can be accommodated. The nature of α-$\rightarrow$$\beta$ phase transformation is reconstructive and it is now generally proved that the process is realized through liquid phase diffusion at the grain boundaries along with densification at high temperatures.
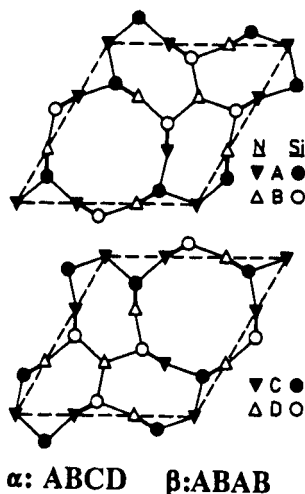
α: ABCD   β:ABAB

Fig. 1 Idealized Si-N layers in α and β silicon nitride: α-structure, ABCD: β-structure, ABAB
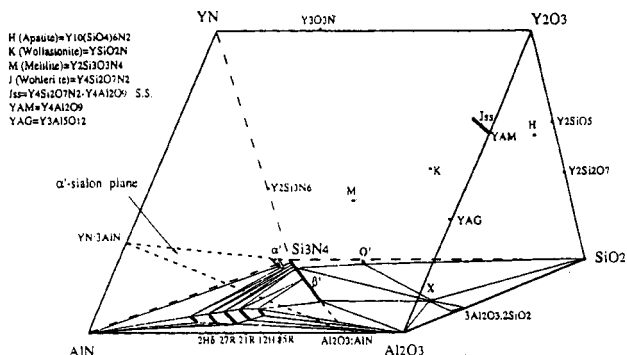
Fig. 2 Representation of Si-Al-Y-O-N behavior diagram in the system and the revised Si-Al-O-N behavior digram

II.2 Phase relationships of the Si-Al-O-N and Y-Si-al-O-N systems

Si-Al-O-N is the most fundamental system upon which another metal atom may be added in the designing and fabrication of most useful nitride materials. The basic Si-Al-O-N system had been a subject of study for over a decade.[5-12] Many complex M-Si-Al-O-N systems (where M = Na, Li, Mg, Ca, Y and rare earth elements) have been extensively studied.[13-27] Among them, the Y-Si-AL-O-N system has been most thoroughly studied,[24,25] especially due to the fact that Al_2O_3 and Y_2O_3 have been shown to be effective additives for the fabrication of silicon nitride ceramics. This quasi-quinary system, 76 compatibility regions (tetrahedra) have been identified in the complete phase diagram is represented by a Janeke prism (Fig. 2).

Much useful information can be extracted from these phase relationship studies. It is now clear that there are several important solid solutions in the systems; β-sialon, α-sialon, O-sialon and AlN polytypoids (Fig. 2) which appear as the major crystalline phase(s) in the silicon nitride materials and show predominating effects on the properties of these materials. β-sialon (or β') is a solid solution of $\beta\text{-}Si_3N_4$, occurring along the line $Si_3N_4\text{-}Al_2O_3$: AlN (Fig. 2) by substituting Al and O for Si and N and keeping the M/X ratio of 3/4 with the general formula $Si_{6-z}Al_zO_zN_{8-z}$. It usually exhibits an elongated prismatic or acicular morphology with aspect ratios ranging from 3-4 to 7-8 or even larger depending on the processing conditions. Both $\beta\text{-}Si_3N_4$ and β-sialon therefore, render the material to have higher strength and fracture toughness. α-sialon is isostructural with $\alpha\text{-}Si_3N_4$ having Al-O and Al-N substituting Si-N and the charge compensation can be realized by a number of metal ions occupying the two large interstitial sites per unit cell. Its general formula is represented at $M_xSi_{12(m+n)}Al_{m+n}O_nN_{16-n}$. This phase occupies an area in the α'-plane as shown in Y-Si-Al-O-N phase diagram (Fig. 2). Many other metal elements have now been identified to form α-sialons. Most α-sialon phases appear to be equiaxed in morphology in nitride materials and are high in hardness with superior thermal shock resistance. O-sialon is the solid solution of Si_2N_2O with Al_2O_3 keeping the M/X ratio at 2/3 (Fig. 2). The solubility of Al_2O_3 in O-sialon is limited, and the O-sialon phase usually possesses good oxidation resistance. The AlN polytypoids usually have an elongated platelet or even fibrous morphology, but their behavior in a compounded microstructure has been much less studied. Besides, a number of compound formation has been identified in these systems.

II.3 Relevant compatible region in the Y-Si-Al-O-N system attractive for materials design purposes

From the above mentioned information, there are about a dozen compatibility tetrahedra out of the 76 compatibility regions in the Y-Si-Al-O-N system that are particularly useful for materials design purposes. Some of the essential considerations are as the following:

β-Si$_3$N$_4$ or β-sialon—Refractory Grain Boundary Phases
α-sialon or α-β-sialon—Refractory Grain Boundary Phases
α-sialon-AlN polytypoids—Refractory Grain Boundary Phases
β-sialon-AlN polytypoids—Refractory Grain Boundary Phases
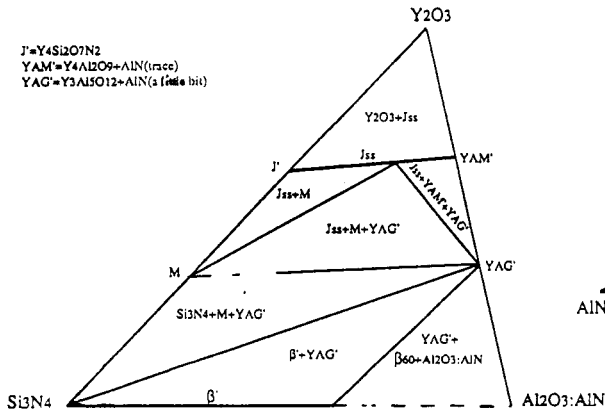O-sialon B-sialon—Refractory Grain Boundary Phases

Fig. 3 Subsolidus phase relationships in the Si$_3$N$_4$-Y$_2$O$_3$-Al$_2$O$_3$: AlN system.
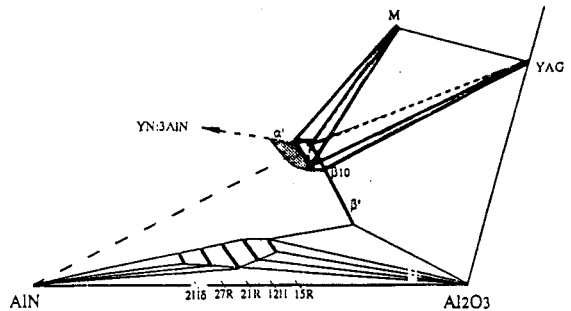
Fig. 4 α'-β' two phase region is compatible with Melilite (M) and YAG forming three compatibility tetrahedra

A few of the potential regions of interest are shown in Fig. 3-5. Fig 3 shows the phase relationships in the Si$_3$N$_4$-Y$_2$O$_3$-Al$_2$O$_3$: AlN system where a large area is available supporting the idea of designing β-Si$_3$N$_4$ or β-sialon materials with yttrium aluminum garnet (YAG)) as the refractory grain boundary phase. To meeting these ends, the factors related with fabrication technology are of equal importance to develop materials with favorable microstructures. For the development of materials with α-sialon or β-sialon as the major crystalline phase(s), the phase relationships shown in Figs.4, 5 can be of use. One can also manipulate around the grain boundary phase(s) as they may appear to be suitable.

II.4 The phase relationships in the Ln$_2$O$_3$-Si$_3$N$_4$-AlN-Al$_2$O$_3$(Ln = Nd, Sm and Dy) systems

The use of rare earth oxides as sintering additives for nitride ceramics has attracted much attention in recent years. They are particularly effective to promote densification either used singly or in combination with other oxides. Besides, for most rate earth elements, they can be absorbed into the α-sialon lattice from the transient liquid after sintering thus reducing the amount of glassy phase at the grain boundaries. Many studies been done on the Ln-Si-Al-O-N systems[28-30] and it is generally known that for heavy rare earth elements, the phase relationships are very similar to those in the Y-Si-Al-O-N system. There are, however, some differences for the light rare earth elements, of which, Sm and Nd are considered to be representative. For instance, there exist two N-containing compounds — Sm(Nd)$_2$AlO$_3$N and Sm(Nd)Al$_{12}$O$_{18}$N (magneto-plumbite, MP compound) and no garnet phase occurs, instead the aluminate, Sm(Nd)AlO$_3$ becomes stable[26]. Light rare earth melilites can also much easily form solid solutions (M',Ln$_2$Si$_{3-x}$Al$_x$O$_{3+x}$N$_{4-x}$) with more Al-O replacing Si-N than the heavy rare earth elements (x=1 for Nd)[31,32] and melilite solid solutions are much more oxidation resistant. Dysprosium is situated near the middle of the rare earth element series. Recent study indicates that it differs from yttrium or samarium in phase relationships in the Ln-Si-Al-O-N system. For Dy, it forms both the garnet phase (DyAG) and the 1:1 aluminate phase (DyAlO$_3$) which is one example. The sub-systems defined by the end-members Si$_3$N$_4$, AlN, Al$_2$O$_3$ and Ln$_2$O$_3$ (Ln=Nd, Sm, and Dy) include α-sialon, β-sialon and AlN polytypoids and many other important member in the system. There are over 40 compatibility regions in each of these subsystems. For the Sm(Nd) system, the compatibility tetrehedra α-sialon-β$_0$-β$_{10}$M'; α-sialon-β$_{10}$-2R-M'; β$_{25}$-β$_{10}$-12H-LnAlO$_3$' β$_{10}$-12H-LnAlO$_3$-M' and β$_{10}$-12H-2lR-M' are the most useful for the design and processing of multi-phase sialon materials. And for the Dy system, there are 5 compatibility tetrahedra involving α-sialon, β-sialon, AlN polytypoids as the major crystalline phase and DyAG and M' as the promising grain boundary phase are of particular interest (see Fig. 6).

III. MATERIALS DESIGN EXAMPLES THROUGH THE HELP OF PHASE RELATIONSHIP UNDERSTANDING

III.1 α-β–sialon composite ceramics with YAG as the grain boundary phase

With the information provided by Fig. 4 and 5, a composite α and β-sialon ceramics was designed with α'/β' = 1/1 ratio and YAG was chosen to be the intergrannular phase.[33] The specimens were first pressureless sintered in N_2 atmosphere to 1800°C. They have attained 97% theoretical density (TD). Then gas pressure sintering was followed to temperatures of 1900°C, 1950°C, and 2000°C respectively under N_2 over pressure. These specimens were all fully densified and the phase compositions of those sintered at 1950°C were determined to be composed of 46 wt% α' and 54% β' with some B-phase and the glassy phase. Most of the specimens were then heat treated at 1350°C for 24 hr to devitrify the intergranular glassy phase. The recrystallized phase is essentially garnet with some n-containing phases. The relative contents of α' and β' phases also showed a slight change. The microstructural development of those sintered at higher temperatures was more dramatic. This was particularly manifested by the grain growth of the acicular β' grains showing larger aspect ratios in a matrix of equiaxed α' grains. The in-situ reinforcement effect of the elongated β' grains in the duplex composite microstructure became evident.
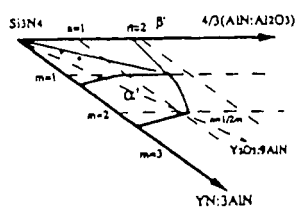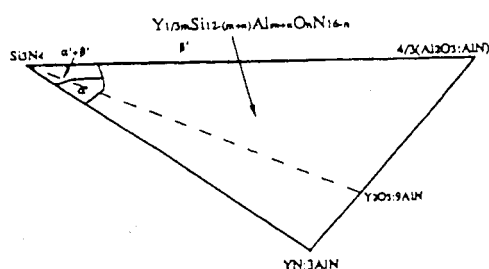

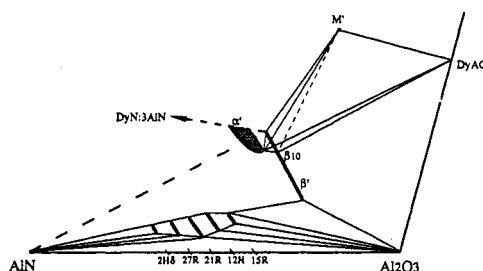Fig. 5 Representation of α-sialon phase in Y-Si-Al-O-N System

Fig. 6 Compatibility terahedra in the Dy-Si-Al-O-N system

Fig. 7 shows their mechanical properties at room temperature. It can be seen that those after the higher temperature, gas-pressure sintering step all show a substantial increase in their mechanical properties. The increase in strength and fracture toughness with advanced processing conditions can be well correlated with the microstructure development. The simultaneous enhancement of strength, fracture toughness and hardness under the GBS processing conditions used in this study is worthy to be noted.

Fig. 8 further shows their flexural strength at high temperatures up to 1350°C. Their strength retention capability at 1350°C was noteworthy. In contrast, the as-sintered material (without heat treatment) showed a drastic drop in strength beyond 1000°C and retains only about one-third of its room temperature strength at 1350°C. Obviously, the nature of the grain boundary phase has played an essential role. From this example, it can be seen that this approach of designing and processing materials with α-plus β-sialon composite major crystalline phases and YAG as the grain boundary phase can be used to produce materials with relatively high strength, fracture toughness, and hardness simultaneously. And their high temperature strength retention capability is also noteworthy. Besides, there is still room for optimization in processing, microstructure development and properties.
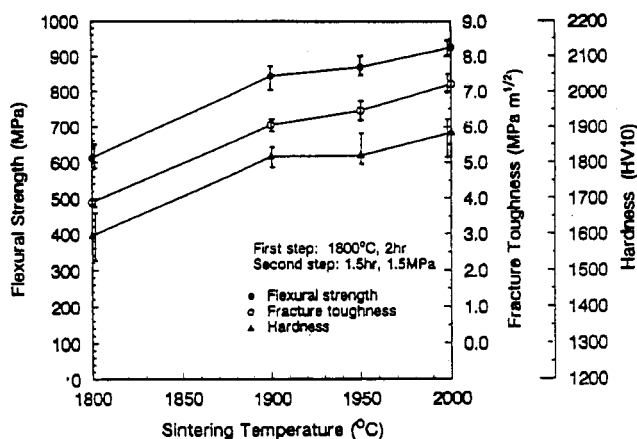
Fig. 7 Flexural strength, fracture toughness and hardness value of specimens: PLS (1800 °C) and GPS (1900-2000 °C, two-steps)
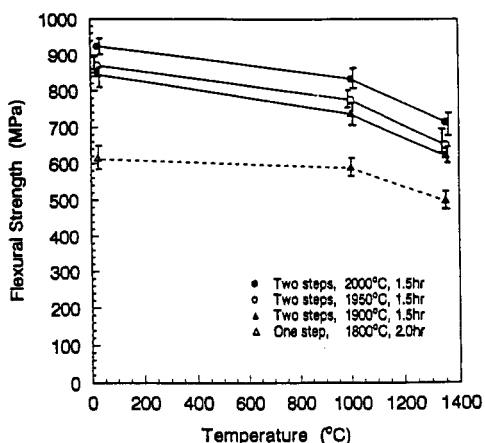
Fig. 8 Flexural strength vs temperature of PLS and GPS specimens

III.2 α-sialon plus AlN composite ceramics

It was shown[24,25] that Y-α-sialon at the oxygen rich end (m=1, n=1.7), 12H (an AlN polytypoid), and YAG are compatible phases. A material of 12H phase alone with a small amount of garnet can be densified by hot pressing[34]. It showed an elongated fibrous (or platelet) microstructure with relatively low strength and fracture toughness.[35] A yttrium α-sialon phase can also be densified with the incorporation of garnet under similar processing conditions and the material has high hardness as is typical for α–sialon materials. This study was intended to show whether the AlN polytypoid (12H) phase by its very microstructure could show any toughening effect in an α-sialon matrix. Some of the results are summarized in Table 1.[36]

TABLE 1 Phase Compositions and Mechanical Properties of α'-12H (Containing 2.5 wt% YAG) Composite Ceramics by Hot-Pressing

Nominal Composition	Phase Composition Determined			σ_f (MPa)	Hv$_{10}$ (Kg/mm^2)	K$_{Ic}$ (MPam$^{1/2}$)
	12H (wt%)	α' (wt%)	β' (wt%)			
α-Sialon	--	89	8	470	1815	6.2
90w/o α' +10 w/o 12H	19	71	7	640	1775	7.2
75w/o α' +25 w/o 12H	41	34	20	520	1700	6.1
12-H	95	--	2	360	1430	3.8

It appears apparent that though the 12H phase by itself is rather weak, its incorporation with an α-sialon matrix can substantially enhance the flexural strength and the fracture toughness of the composite material without impairing its hardness to any noticeable extent. To the authors knowledge, this is the first indication that an AlN polytypoid phase can perform a toughening as well as a strengthening role in a nitride composite.

III.3 Dy$_2$O$_3$ densified α-sialon and β-sialon ceramics

From the study of Dy-Si-Al-O-N system,[37] it has been shown that both α-sialon and β-sialon are compatible with the garnet phase (DyAG) and the melilite solid solution phase (M'). Therefore, either DyAG or M' can be designed as the grain boundary phase for Dy-sialon ceramics. Moreover, as a member of the rare earth element series, Dysprosium is situated at the central position. Dy$_2$O$_3$ has, thus the advantage of being effective as an additive for the densification of silicon nitride ceramics as other rare earth oxides. And yet the α-sialon phase doped with Dy has proved to be much more stable than the Sm(Nd)- α-sialons during heat treatment.[38] Therefore Dy$_2$O$_3$ densified sialon ceramics should be favorable candidates for application. The following are a few recent examples with Dy$_2$O$_3$ as the sintering aid.

By designing α-sialon composition at $Dy_{0.33}Si_{9.3}Al_{2.7}O_{1.7}N_{14.3}$ with different amounts of DyAG, the starting powders were carefully processed and sintered into fully dense specimens by hot-pressing at 1800°C for 1 hr. Table 2 shows some of results.[39]

TABLE 2. α-Sialon with Different DyAG Contents

Sample No.	DyAG Content (wt%)	Phase Compositions As Sintered			Density (g/cm^3)	Mechanical Properties		
		α'	β'	G		σ_f (MPa)	Hv_{10} (Kg/mm^2)	K_{1c} (MPam$^{1/2}$)
A-0	0	90	10	--	3.42	600±20	1860	5.4
A-1	2.5	100	0	--	3.45	580±18	1850	5.2
A-2	5.0	100	0	--	3.47	530±25	1760	5.1

From these results, it can be seen that even without the addition of garnet in the form of Dy_2O_3 and Al_2O_3 in sample A-O, the material can be densified by hot pressing. Apparently, the liquid phase formed between the oxides before the complete formation of the α-sialon phase is capable to realize full densification. And due to the fact that a part of Dy_2O_3 is taken up in the liquid phase, some β-sialon has occurred in the designed stoichiometric α-sialon composition. The mechanical properties of these materials show that being fully densified, those with less grain boundary glassy plane favor higher strength and hardness. The α-sialon material with 5 wt% addition of DyAG significantly weakens the flexural strength and lowers the hardness value. By heat treatment of the samples at 1450°C, garnet phase was identified to crystallize out at the grain boundaries. The studies on their mechanical properties, especially those at higher temperatures are still ongoing and would be of interest to pursue.

β-sialon material and α-plus β-sialon composite material using Dy garnet as the grain boundary phase have also been designed and investigated.[40] α-sialon has the same composition as that mentioned above. $\beta'_{10}(Si_{5.2}Al_{0.8}O_{0.8}N_{7.2})$ was selected as the β-sialon phase.

TABLE 3. β-Sialon and α- plus β-Sialon Composite with DyAG Additive

Sample No.	Composition Designed			As Sintered			HT 1450°C -72 hr			Density g/cm^3	Mechanical Properties K_{1c} MPam$^{1/2}$	Hv_{10} Kg/mm^2
	α'	β'	G	α'	β'	G	α'	β'	G			
B-2	–	95	5	.15	85	–	–	100	w	3.24	6.8	1630
AB-1	65	30	5	85	15	–	65	35	w	3.38	5.8	1770
AB-2	30	65	5	50	50	–	30	70	w	3.30	5.9	1670

It is evident that α-sialon had a higher priority to be formed during sintering in favor of garnet phase or the melilite phase. However, during post-sintering heat treatment, garnet phase crystallized out consuming the dysprosium content from the intergranular glass thus promoting the decomposition and transformation of the α-sialon into the β-sialon phase. And eventually the designed α-β-sialon composite composition was attained after heat treatment at 1450°C. The mechanical properties of the as-sintered materials reflected the microstructure of the morphologies of different phase compositions. Composition B-2 with very high β-sialon content showed a high k_{1c} value and lower hardness. While compositions AB-1 and AB-2 showed the in-situ toughening effect through the presence of β-sialon in a matrix of equiaxed α-sialon phase. And the α' phase content also contributed to the higher hardness values of the composites.

The enhancement of material composition design capability through the use of the knowledge from multicomponent phase relationship studies is evident. This approach is still at its beginning stage and more fruitful results can be expected, especially while the kinetic factor is taken into consideration. It is well known that microstructural development and control are equally important in the tailoring of properties as has also been manifested to some extent in this paper. In this respect, the in-depth study and application of advanced processing technology can be a powerful tool and will play an essential role.

ACKNOWLEDGMENT

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