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Material chemistry studies—their role for the development of advanced nitride materials

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Abstract: In this paper, the role of material chemistry for the synthesis and processing of advanced materials is addressed. Advanced nitride materials, essentially those that may be generated within the complex Si-Al-Y-N-O system have been chosen to illustrate the two issues that material chemistry studies are important. These are: (1) the phase compositional design of materials guided by a detailed knowledge of the phase relationships of these complex systems; and (2) the kinetics related with the processing of silicon nitride solid solution — Sialon composites and its influence on microstructure development. It is aimed to explore the potential of these material chemistry approaches by some examples studied in this Lab. It is also relevant to note that significant advancements can be expected through close collaboration between chemists, physicists, and materials scientists and that is what is called for in the Age of Materials.

Key Words: Material Chemistry, Advanced Nitride Ceramics, Phase Equilibrium Relationships, Reaction Kinetics, Sialon Formation

Introduction

As generally anticipated, the nineties and the first part of the 21st century will be a period of high growth rate with technology as the central core for economic development. It is also commonly recognized that materials science and engineering and new materials will be one of the few cornerstones for such development. And advanced inorganic materials will have an even faster pace of development in comparison with other types of new materials.

Speaking of materials science and engineering(MSE), it can be reasonably delineated into the following essential elements: synthesis and processing, composition and structure (including microstructure), properties, and performance.[1] These elements are closely interrelated. It is, therefore, evident that MSE is highly multidisciplinary and interdisciplinary in its inherent contents of research. Chemistry, physics, mathematics and many engineering disciplines are heavily involved when one embarks on the study of the above mentioned elements of MSE. And chemistry is the main discipline concerned for the investigation on synthesis and processing leading to a certain structure (including microstructure) of the material with a prescribed composition. The properties of ceramics materials are sensitively affected by processing since it controls to a great extent the content and grain sizes of different phases and the shape and amount of defects in the material. For high performance ceramics, actually the entire processing steps from fine powder preparation, green compact formation through to the finally sintered body have a great deal of influence on the microstructure, defects and properties of the material. Most fine powders, especially ultrafine powders are prepared through chemical routes. On the other hand, the properties of ceramics

strongly depend on the compositions, since the phases present, both the matrix phases and grain boundary phases, are, in a way, dictated by the compositions and may possess very different characteristics. Therefore, optimum tailoring of phase compositions and microstructure can significantly control the material properties aiming at different application requirements. This is a very fertile field of research as can be easily seen when present day technology asks for good, reliable materials having consistent performance under stringent conditions of application.

With this understanding, I am trying to address to our chemistry community on the topic of materials chemistry by using nitride ceramics as a model system to illustrate how a pivotal role can be played through such studies for the development of advanced nitride materials.

Some Remarks on Nitrite Ceramics

Advanced nitride ceramics is a family of materials that has exhibited extremely encouraging properties especially those at high temperatures. Among nitride ceramics, silicon nitride ceramics is the most promising group of materials for high performance engineering applications, and itself, is also a materials family. From structural chemistry point of view, the fundamental building units for silicon nitride materials are $[SiN_4]$ and $[(Si,Al)(N,O)_4]$ tetrahedra which are similar, in a way, to the silicate materials family with $[SiO_4]$ as the basic building unit. One essential difference between these two materials families stems, however, from the highly covalent nature of the Si-N bond in silicon nitride ceramics which leads to very low diffusivity of either Si or N even at very high temperatures. The excellent properties of silicon nitride ceramics are apparently attributed to this feature. But, consequently, additives, essentially oxide additives are necessary to achieve full densification through liquid phase sintering, since good mechanical properties of structural ceramics can usually be obtained in fully dense materials. Therefore, the compositional design of nitride ceramics leaves an open room for materials chemistry studies in the development of potentially attractive materials.

Si_3N_4 has two different crystalline polymorphs, α-Si_3N_4 and β-Si_3N_4[2-6]. Their fundamental 3-dimensional network structure is composed of $[SiN_4]$ tetrahedra with three of them sharing one N atom. the difference in the stacking of Si-N layers for both α- and β-Si_3N_4 is shown in Fig. 1a and Fig. 1b and their structural parameters are summarized in Table 1[2,6]. Each unit cell of α-Si_3N_4 has 4 molecules with Si-N layers stacked in ABCD order thus having two large holes in the structure which can accommodate large sized ions. The β-Si_3N_4 has two molecules in each unit cell with the Si-N layers stacked as ABAB. The actual β-Si_3N_4 structure is very close to that of the ideal one while in α-Si_3N_4, there are slight movements of N atoms at 3/8, 7/8 positions towards the centers of the holes(can be seen from Fig. 1b).

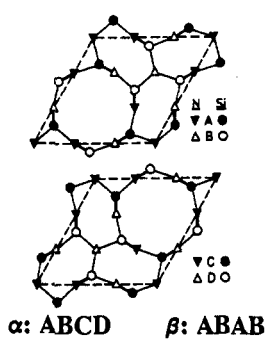

Fig.1a Idealized Si-N layers in α and β silicon nitrides: α-structure, ABCD, β-structure, ABAB

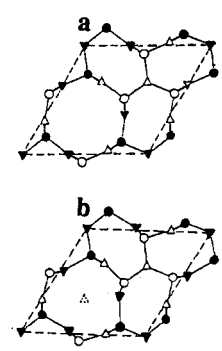

Fig.1b Actual Si-N layers in α and β silicon nitride: a, in β-Si_3N_4; b, in α-Si_3N_4

Table 1 Structural parameters of α-Si_3N_4 and β-Si_3N_4

	α-Si_3N_4	β-Si_3N_4
Space Group	P31c	P63/m
Cryst. system	Hexagonal	Hexagonal
Unit Cell Dimensions (Å)	a=7.753 c=5.618	a=7.608 c=2.911
Stacking of Si-N Layers	ABCD	ABAB
Density (g/cm^3)	3.183	3.192

The phase transformation from α-β is reconstructive in nature and it is now the general consensus of opinion[8-10] that the process is carried out through the liquid phase formed essentially between the oxide additives at the grain boundaries along side with densification at high temperatures.

Thermodynamics of Complex Nitride Systems — Phase Equilibrium Relationship Studies and their Role in Materials Design

Since oxide additives are necessary and are commonly incorporated in the composition for the fabrication of advanced nitride ceramics, the thermodynamics of such complex nitride systems is of major concern with the focal point on their phase equilibrium relationship understandings[11-17]. The basic Si-Al-O-N system had been a subject of study in the seventies(Fig. 2). Many complex M-Si-Al-O-N (M=Na, Li, Mg, Ca, Y, and rare earth elements) systems have been extensively studied in more recent years[18-31]. It is now clear that there are several important solid solutions in these systems: β'-Sialon, α'-Sialon, O'-Sialon and AlN polytypoids (Fig. 3) and each has its own typical crystalline morphology and physical characteristics. β'-Sialon is a solid solution of β-Si_3N_4, occurring along the line Si_3N_4 — Al_2O_3: AlN by keeping the M/X ratio of 3/4 without creating point defects with the general composition $Si_{6-z}Al_zO_zN_{8-z}$ and $O<Z<4.2$(Fig. 2). It exhibits a prismatic or acicular morphology with aspect ratios ranging from 2-3 to 7-8 or even larger depending on the processing conditions. Both β-Si_3N_4 and β'-Sialon have higher strength and fracture toughness. Microstructures with in-situ growth of β'-Sialon can be expected to have self-strengthening and especially toughening effects. α'-Sialon is isostructural with α-Si_3N_4. Its general formula can be represented as $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, where m(Si-N) are substituted by m(Al-N), n(Si-N) by n(Al-O) with valency discrepancy being compensated by some metal ion M occupying the two large isolated interstices in the α-Si_3N_4 structure. Many metal elements have been shown to form α'-Sialons and those identified upto the present are Li, Ca, Y, and rare earth elements starting from Nd[23,25,29]. All α'-Sialons have an equiaxed morphology. O'-Sialon is the solid solution of Si_2N_2O with Al_2O_3 keeping the M/X ratio at 2/3. The solubility of Al_2O_3 in O'-Sialon is limited and has still some discrepancies between different authors[14,17,33,37]. The characteristics of these Sialons can be briefly summarized as follows: O'-Sialon possesses better oxidation resistance; β'-Sialon, high fracture strength and toughness; and α'-Sialon, high hardness and better thermal shock resistance. AlN-polytypoids usually have an elongated platelet or even fibrous morphology, but their behavior in a compounded microstructure has been much less studied and less known. Besides, a number of new compound formation has been identified in these systems. The significance of phase relationship studies of silicon nitride system is thus, to provide information for: (a) the search and selection of effective sintering additives to achieve densification; (b) the design of nitride ceramics with desirable major phases; and (c) the control and tailoring of grain boundary phases. Therefore, the possibility for compositional design of such multiphased materials on a more scientific basis to better meet with different application requirements has been a subject of intensive research in recent years.

Y-Si-Al-O-N is the system that has received the most close attention since Al_2O_3 and Y_2O_3

were shown to be effective additives for silicon nitride ceramics. Within this multi-component system, 76 compatibility regions have been identified after around ten years' work in close collaboration with several world renowned laboratories (Fig. 3) [30,31]. Among them, there are about a dozen which are of particular interest to serve as the basis for the compositional design of high performance materials, especially those with duplex Sialon phases to take advantage of the favorable characteristics of these different phases. A few promising combinations are as the following:

βSi_3N_4 or β'-Sialon — Refractory Grain Boundary Phases
α'-Sialon or α'-β'-Sialon
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 — β'-Sialon — Refractory Grain Boundary Phases

Some of these potential regions are illustrated in Fig. 4-6.

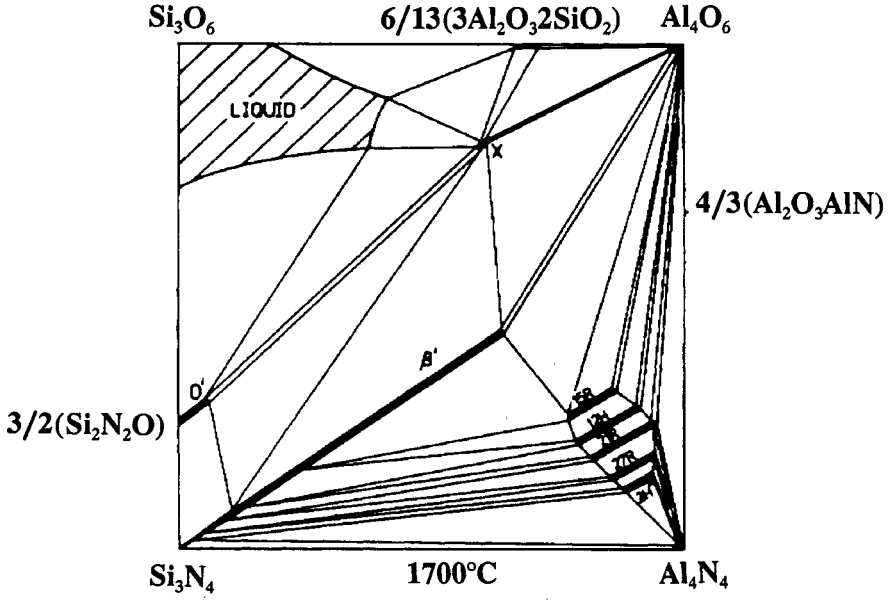

Fig.2 Phase relationship of Si-Al-O-N system at 1700°C

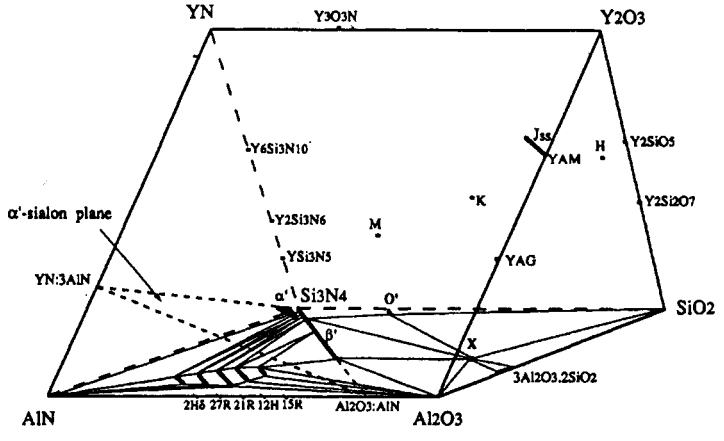

Fig.3 The sub-solidus phase relationships of Y,Si,Al/O, N system showing the solid solutions and AlN polytypoids

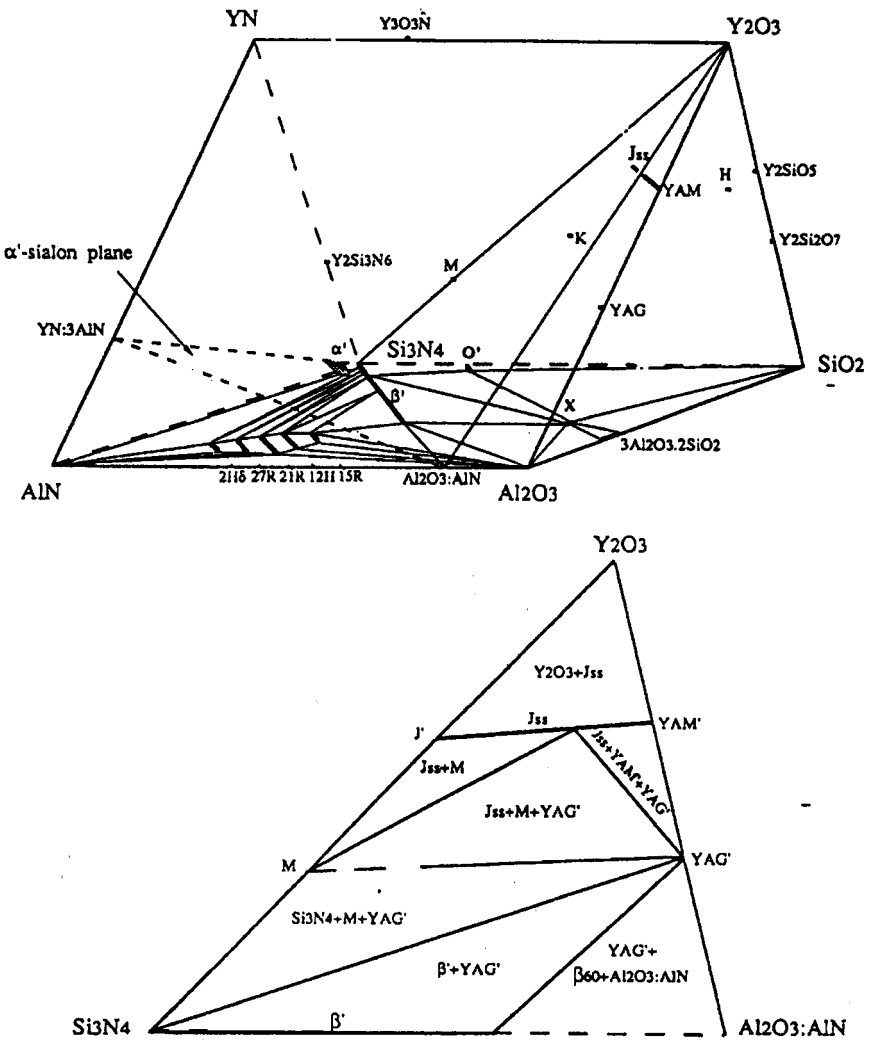

Fig. 4 Sub-solidus phase relationships in the Si_3N_4-Y_2O_3-Al_2O_3:AlN System[18]

A couple of examples will be enumerated to show the effectiveness of such an approach for materials compositional design.

The first example deals with a βSi_3N_4 or β'-Sialon material and focus the attention to upgrade the grain boundary phase (or phases). When using Y_2O_3 and Al_2O_3 as the compound additive for sintering, the glassy phase formation temperature starts at the eutectic temperature of SiO_2-Al_2O_3-Y_2O_3, which is 1350°C. By deleting Al_2O_3 and using Y_2O_3 plus La_2O_3 or another rare earth oxide as compound additives, the lowest eutectic temperature can be raised by some 200°C[37,38]. The glassy phase that remained at the grain boundaries after sintering will be much more refractory. Moreover, post-sintering heat treatment under ordinary atmospheric conditions will devirtify or partially devirtify to form $LaYO_3$ crystalline phase along with other N-containing phases as shown by our experiments and the sub-solidus phase relationships in the system Si_3N_4-Y_2O_3-La_2O_3 (Fig. 7). The comparison of the mechanical properties of these two types of β-Si_3N_4 (or β'-Sialon) material is obvious and the material with compound Y_2O_3 and La_2O_3 additive can retain its flexural strength up till 1300°C (Fig. 8). By manipulating the additive contents to keep the average grain boundary thickness at 4 and 8 nm, the flexural strength retention of the material up to 1400°C or somewhat beyond has been achieved (Fig. 9)[39]. The creep property of these materials has also been studied.

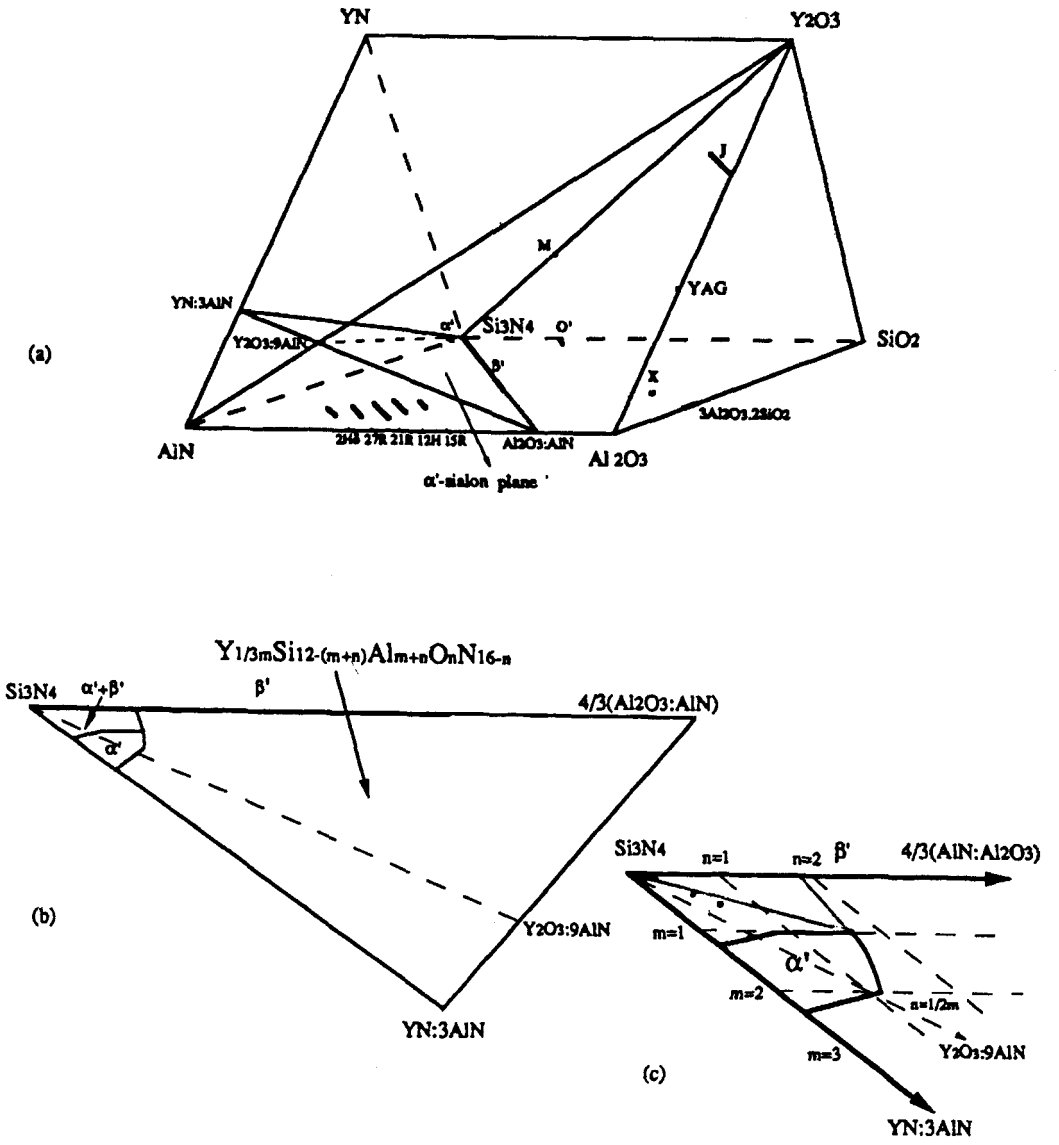

Fig. 5 Representation of α'-Sialon phase in Y-Si-Al-O-N system[31]

Apparently, the ones with 4 nm grain boundary width show a noticeably lower creep strain at 1300°C under 250 MPa stress up to 200 hrs (Fig. 10). The mechanism of creep has been preliminarily investigated. At very high temperature (say 1400°C) and high stress, cavitation has been identified to play a major role, otherwise, diffusional mechanism appeared to be controlling, especially for specimens with very thin grain boundary thickness.

As mentioned before, the multiphase ceramics may offer the possibility to tailor the microstructure and properties by making good use of the characteristics of each phase. The second example is to show the strengthening effect of AlN polytypoid in a matrix of α'-Sialon [31]. Table 2 shows some of the data obtained on the α'-12H composite material [40].

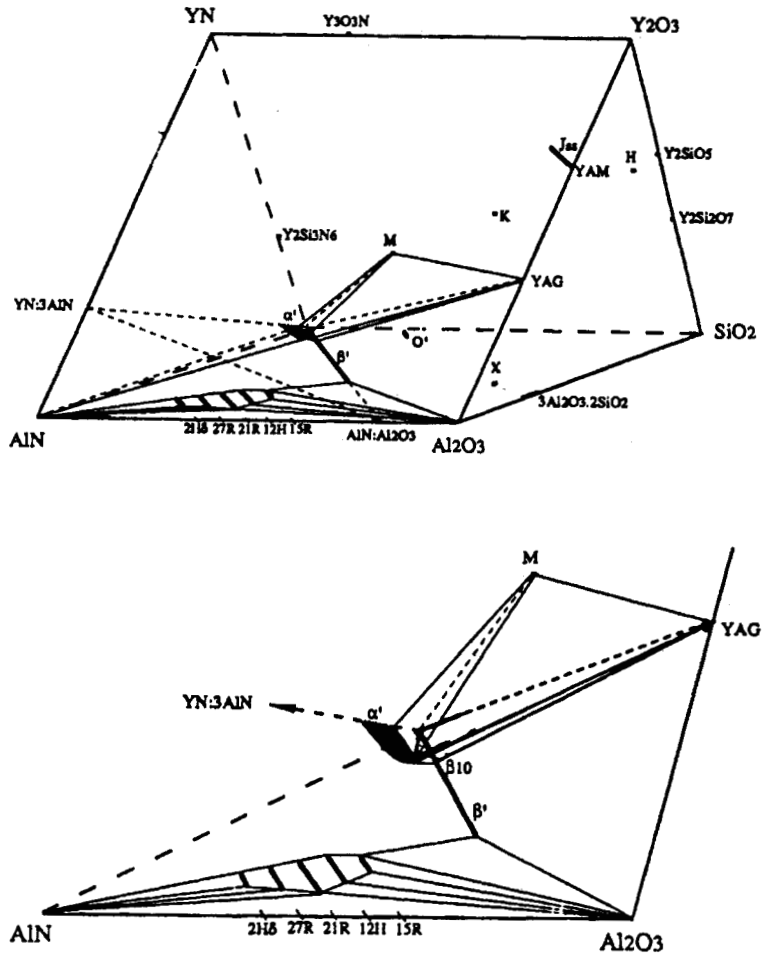

Fig. 6 α'-β' two phase region with melilite (M) and garnet (YAG) phases

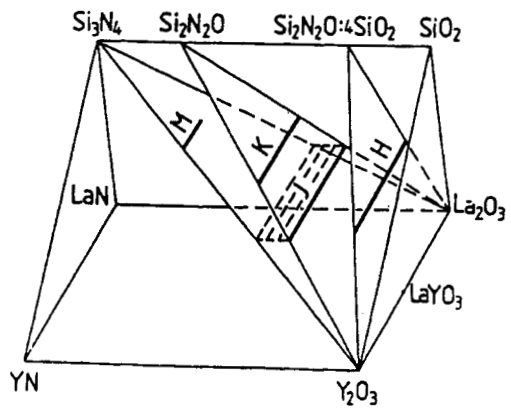

Fig.7 Sub-solidus phase relationships in the system Si-Y-La-O-N

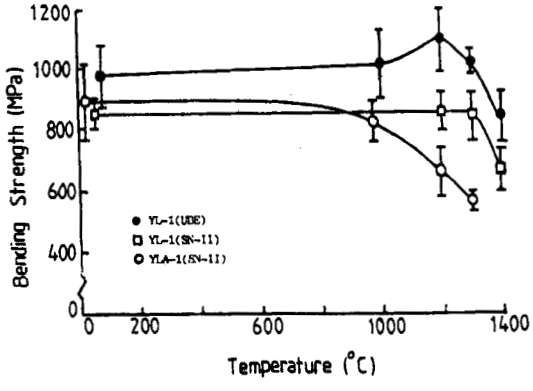

Fig.8 Bending Strength vs Temperature of YL-1 and YLA-1

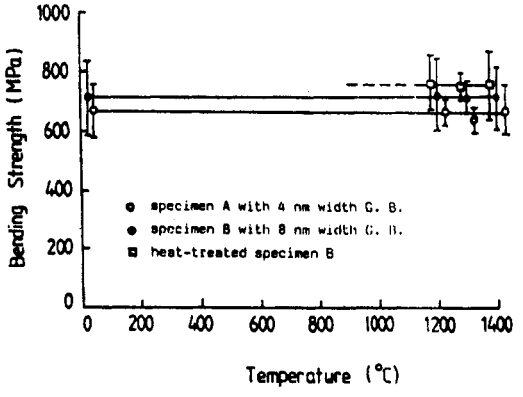

Fig. 9 Bending Strength vs Temperature relationship of specimens with controlled G.B. Width

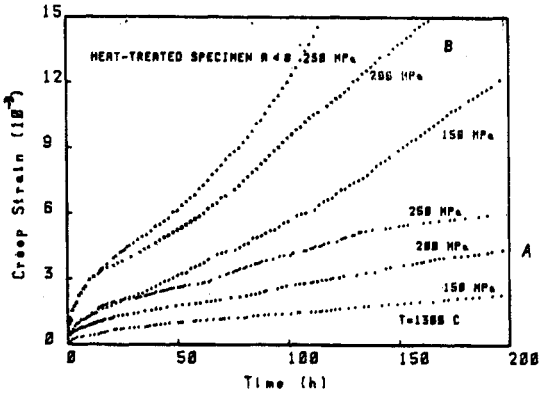

Fig.10 The relationship between creep rate and applied stress

Table 2 Phase compositions and mechanical properties of α'-12H (containing 2.5 w/o YAG) composite ceramics hot-pressed at 1750°C, 1h

Nominal Composition	σ_f (MPa)	H_{v10} (kg/mm^2)	K_{1c} (MPa.m$^{1/2}$)	12H wt%	α' wt%	β' wt%
α'-Sialon	470	1815	6.2	nil	89	8
90w/oα'+10w/o12H	640	1775	7.4	19	71	7
75w/oα'+25w/o12H	525	1700	6.1	41	34	20
12H	364	1430	3.8	95	nil	2

Apparently, 12H phase, by itself, is rather weak and α'-Sialon, as expected, is very hard. The incorporation of ~20 wt% of 12H phase (nominally 10wt%) with an α'-Sialon matrix substantially enhances the flexural strength as well as the fracture toughness of the composite material without impairing its hardness to any appreciable extent. To the author's knowledge, this is about the first indication that an AlN polytypoid phase can perform a strengthening as well as a toughening role in a nitride composite. It should be interesting to further pursue the strengthening mechanism underlying this type of composite materials.

Kinetics Related with the Processing of α'- and β'-Sialon Composite and Its Bearing on Microstructure Development

Under the guidance of the information extracted from phase relationship studies of multi-component systems, compositional design can be attempted with reasonable success as enumerated in the previous section. It is intended to elaborate slightly further in this passage the kinetic side of the problem related with material processing at high temperatures. In a way, it is of no less importance in dictating the phases that actually present in the material and their microstructure and thus affecting the properties.

By high temperature processing of a material with a certain designed phase composition, the reactions that occur at different temperature stages are generally complex. They may occur consecutively, concurrently, or overlapping one with the other. An overall analysis is usually what a material scientist would like to do to help understanding the general situation for complicated systems. We will address this issue in the following passage by studying α'-Sialon plus β'-Sialon

composites with a nominal weight ratio of 50:50. As understood from the phase relationships of Y-Si-Al-O-N system[31], the oxygen rich α'-Sialon (m=1, n=1.7) is compatible with β'-Sialon (from β_o to β_{10}). It is also understood that rare earth elements from Nd upwards can be incorporated into the α'-Sialon structure. The composition designed in this study for β'-Sialon is β_{10} represented as $Si_{5.23}Al_{0.77}O_{0.77}N_{0.23}$ and that for α'-Sialon is m=1 and n=1.7 corresponding to $Re_{0.33}Si_{9.3}Al_{2.7}O_{1.7}N_{14.3}$, while Re=Sm, Dy, Yb, etc. By taking into consideration of the surface oxides on the Si_3N_4 and AlN powders used (each containing 1.5 w/o O), the weight percentages of various starting materials are calculated and shown in Table 3

Table 3 The Wt. Percentages of Starting Materials for 1:1 α'-plus β'-Sialons

Rare Earth	Si_3N_4	AlN	Al_2O_3	Sm_2O_3	Dy_2O_3	Yb_2O_3
Sm	79.100	10.505	5.099	4.750		
Dy	78.866	10.456	5.086		5.047	
Yb	78.666	10.414	5.074			5.303

These powder mixes were ground and mixed by ball milling for 24 hrs. in an alumina jar with well sintered silicon nitride balls in a medium of absolute alcohol. After drying, these powder cakes were loosely disintegrated and sieved and then dry pressed into bar specimens under 20MPa and finally isostatically pressed under 200 MPa.

Two groups of sintering or densification experiments were carried out[41]. These were (1) sintering with constant temperature rise and (2) by bringing the specimen rapidly to a specified high temperature and sintering followed with time.

1. Sintering of Re-Sialon Composites under Constant Temperature Rise

The sintering experiments were carried out under 10 atm N_2 pressure and a high temperature dilatometer was designed and operated in the pressure chamber where the length change can be monitored and recorded. The temperature rise was maintained at 10°C/min. The shrinkage and shrinkage rate of different rare earth Sialon composites are plotted against temperature as shown in Fig. 11, 12. And some of the results are summarized in Table 4.

Table 4 Some Results of Gas Pressure Sintered Re-Sialon Composites by Constant Temp. Rise to 2000°C

Sample	Sm-Sialon Composite	Dy-Sialon Composite	Yb-Sialon Composite
Density (g/cm^3)	3.12	3.11	3.11
Rel. Density (% Theo.)	95.2	94.2	93.9
Starting Shrinkage at (°C)	~1140	~1180	~1250
Max. Shrinkage Rate at (°C)	1475	~1550	~1600
Max. Shrinkage (%)	19.8	17.8	17.7

The processes that go along with temperature rise can be envisaged as: the formation of lowest melting eutectics between oxide constituents with the help of impurities that are unavoidably present; limited particle sliding and rearrangement in the compacts when glassy phase starts its formation at grain boundaries; dissolution of the nitride compounds in the glassy phase; mass

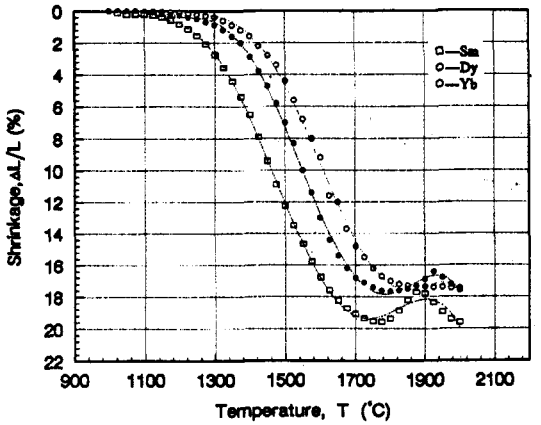

Fig.11 Temperature dependence of shrinkage of different rare earth Sialon composites

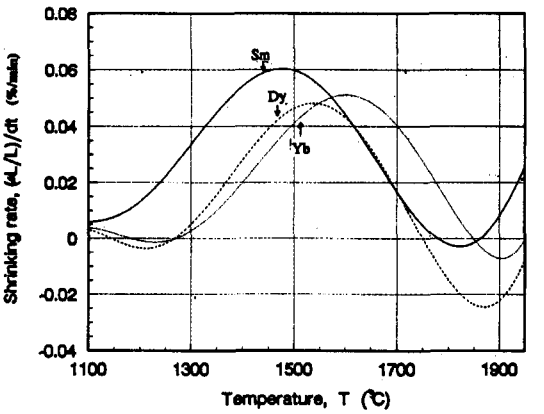

Fig.12 Temperature dependence of shrinkage rate of different rare earth Sialon composite

transport through the grain boundary glassy phase by solution, diffusion and precipitation; phase transformation of α-Si_3N_4 to β-Si_3N_4; resorption of different ionic species from the glassy phase to form α'-Sialon and β'-Sialon. Most of the processes lead to densification and are kinetic in nature that are manifested by shrinkage in the dilatometer arrangement. It is difficult to separate these processes, since they overlap and are interwovenly mingled together. But some experimental data may help to explain the phenomena as assembled in Table 4. Experiments have shown that the amount of glassy phase formed by adding Sm_2O_3, Dy_2O_3, or Yb_2O_3 as additives decreases in the above order. And the nitrogen content dissolved in the glassy phase increases following the same order. As determined by Parallel Electron Energy Loss Spectroscopy (PEELS), the N contents in the glassy phase represented as atomic ratios of N/O are 0.17 for Sm-Sialons and 0.43 for Dy-Sialons. Apparently, higher glassy phase content with lower dissolved nitrogen concentration and thus having lower viscosity in Sm_2O_3 containing Sialon composite material can qualitatively explain many of the above mentioned processes that start to proceed at relatively lower temperatures and at a higher rate kinetically in comparison with those using Dy_2O_3 or Yb_2O_3 as sintering additives. Higher glassy phase contents favour the development of prismatic β'-Sialon phase with larger aspect ratios. This microstructural feature leads to higher fracture toughness. However, rare-earth ions with higher atomic numbers help to form more α'-Sialon phase. But a fair proportion of rare-earth elements remains in the glassy phase. Some of these information are summarized in Table 5.

Table 5 Phase Composition, Microstructure and Properties of Re-Sialon Composites

Sialon Composite Samples	Sm-Sialon	Dy-Sialon	Yb-Sialon
$\alpha'/(\alpha'+\beta')$	15.2	21	27
Aspect Ratio of β'Sialon	6-8	5-6	3-4
K_{1c} (by Indentation) $MPa.m^{1/2}$	6.4	5.8	4.7

2. Constant Temperature Sintering of Re-Sialon Composites

In this group of experiments, green compacts of Sialon composites similarly fabricated (with nominal α- to β'-Sialon Wt. ratio 50:50),containing different rare earth oxide additives, were quickly heated up to a predetermined temperature. Then their sintering rates were followed at that

temperature. Fig. 13 shows the Log-Log plot of shrinkage with time of Sm, Dy and Yb doped Sialon materials at 1500°C. For liquid-phase sintering as proposed by the Kingery model[43] under the mechanism of solution-diffusion-precipitation, the rate controlling process can be identified by the value n in the following equation:

$$\frac{\Delta L}{L} = kt^{\frac{1}{n}}$$

where K is a value involving such parameters as temperature, liquid film thickness, and coefficient of diffusion in the liquid phase etc, t is time. And the value of n symbolizes the rate controlling step in the solution-diffusion-precipitation processes. However, it is also a shape dependent factor. For prismatic and acicular particles, a value of 3 for n indicates that solution-precipitation is the rate-controlling step, and n=5 suggests that the diffusion step is rate-controlling. Apparently, for these Sialon composites, the β'-Sialon phase is predominating (Table 5)[42] which shows an prismatic morphology.

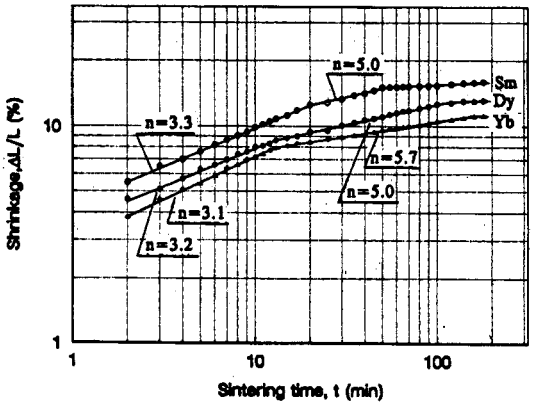

Fig.13 Log-log plots of shrinkage of different rare earth Sialon

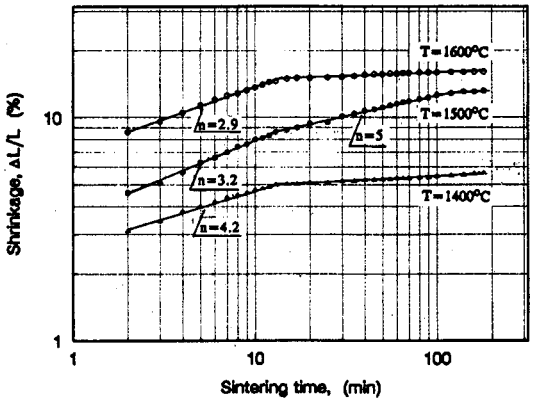

Fig.14 Log-log plots of isothermal shrinkage of Dy-Sialon composites at different temperature

From Fig. 13, there are two kinks on the respective curves. For the first 10-20 minutes (the first stage), while nitrogen dissolution in the glassy phase is still low, n values are close to 3 for all three kinds of rare earth doped sialon composites indicating that kinetically, solution and precipitation is the rare controlling step. In the 2nd stage, all the curves give n values close to 5. This may be explained by the increase in viscosity of the glassy phase after reaching the limit of nitrogen solubility and the rate-controlling step turned to be diffusion.

Experiments with Dy_2O_3 doped Sialon composites were further performed at 1400°C and 1600°C respectively (Fig.14). The n values obtained seem to reflect what would have been expected. At a lower temperature of 1400°C, the controlling mechanism of densification appears to be mixed (with n=4.2) due to the higher viscosity of the glassy phase. While at a higher temperature of 1600°C, it seems that solution-precipitation is essentially controlling all the way leading directly to a more advanced degree of densification. It may, in general, be concluded that the Z value of the rare earth element and the amount and characteristics of the glassy phase formed at high temperatures govern the rate of densification, the development of microstructural features and thereon the properties of the Sialon composite materials.

Concluding Remarks

The role of material chemistry studies for the development of advanced materials has been

discussed in this paper. Advanced nitride materials, essentially those within the complex Si-Al-Y-N-O system, have been chosen to illustrate the two important issues that material chemistry can play. They are: (1) the thermodynamics of complex nitride systems and their contribution in materials design; (2) kinetics related with the processing of Sialon composites (silicon nitride solid solutions) and its bearing on microstructure development. Some examples have been enumerated which indicate the potential of such approaches for the development of promising, high performance materials. Close collaboration between chemists and materials scientists are thus encouraged to meet with the challenges in the nineties and beyond.

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