Role of liquid sintering aids in the synthesis of SiAlON materials

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Abstract

The synthesis of dense sintered sialon with external additives selected from the system Y_2O_3-AlN-SiO_2 is described. The highest density (3.21g/cc) was achieved at 1750ºC at 90 min of sintering with 5 wt% additive. Non-oxide ceramic materials are increasingly coming out as a potential candidate in engineering applications and among them, sialon is one of the most important materials.

β-Sialon was first to be discovered in this class of compounds. It has an excellent combination of thermal, mechanical and chemical properties. The degree of sialon substitution increased with the amount of liquids, the $YSiO_2N$ crystalline phase formed concurrently. Strength degradation occurred above 1000ºC.The fracture toughness of the material sintered with a lower amount of sintering aid remained relatively unchanged to 1200ºC.

Keywords: Sialons, hot pressing, isostatic pressing, sintering, garnet, oxynitride.

Introduction

Sintering of sialon with external sintering aids has been expressed. A liquid composition in the system Y_2O_3-Al_2O_3-SiO_2 was used which on crystallization produced a silicon-substituted "yttrium-garnet" of the general composition $Y_6Al_{10-x}Si_6O_{24-x}N_x$[25].

In this phase, the excess silicon from the secondary glass composition diffuses into ß - sialon, hence decreasing its residual glass or substitution level. Sintering with low amount of Y_2O_3 has been studied, it was observed that this new stoichiometry required the addition of some additive or the presence of impurities for densification[1].Y_2O_3 was observed to promote sintering by the formation of a liquid silicate which remained in the grain boundary instead of entering into the ß-sialon structure. It was shown that a nitrogen rich liquid from the system Y_2O_3-AlN-SiO_2 can be used successfully to sinter Si_3N_4[26]. It also aids the precipitation of $3Y_2O_3.5Al_2O_3$ from green boundary glass.

Hence the nitrogen rich glass is more refractory. ß- sialon with a lower degree of substitution had much mechanical properties but it was more difficult to sinter than that with the higher values of 1.0 and 2.0[6]. Oxinitride glass introduced by incorporating SiO_2 into the batch resulted in thermal decomposition at the firing temperature. Engineering applications such as turbine components, ball bearings, and hard cutting tools require the use of materials that exhibit high strength, toughness and hardness, exceptional thermal performance, high resistance to oxidation, wear, and corrosion.

Silicon nitride (Si_3N_4) is a ceramic material that has been extensively used in areas requiring exceptional mechanical properties at elevated temperature such as gas turbine engine parts[20]. Sintering silicon nitride material led to the development of sialon materials, where Si_3N_4 structure is modified by replacing a fraction of the silicon (Si) and nitrogen (N) with aluminum (Al) and oxygen (O)[8,20]. Sialonis is a solid solution of Si_3N_4 and Al_2O_3.[20,21,29] Sialons could primarily exist in two major phases:alphaor beta.[9,10,14,20,27,29]

The β-sialon, developed during the 1960s, is represented with the general formula of $Si_{6-z}Al_zO_zN_{8-z}$ where $0 < z < 4.2$. The α-sialon, which was developed later on, is represented by $Me_{m/v}Si_{12-(m+n)}Alm_{+n}O_nN_{16-n}$ where 'Me' could be a rare-earth metal (Ln), an alkaline earth metal (Mg, Ca etc.), or a metal belonging to the alkali group (Li). The 'm' and 'n' values represent the (Al–N) and (Al–O) bonds which substitute the (m+n):(Si-N) bonds and 'v' represents the valency of cation 'Me'[9]. The performances of α- and β-sialons have been studied extensively, and they have been discussed mainly based on their microstructure–property relationship. The elongated grains in β-sialon are responsible for their improved fracture toughness and similarly, the improved hardness of the α-sialon is attributed to their equiaxed morphology[11]. It is desirable to obtain α-sialons with high fracture toughness, and this has been achieved in several studies[30,31].

Various reinforcements and additives such as cubic boron nitride (cBN)[18,19], Ca metal[2,3,22], Al metal[4],AlN[33], SiC[22]and rare-earthoxides[23,32,34] have been used to reinforce α-sialon composites with improved fracture toughness .Silicon nitride and oxynitride ceramics have attracted interest for high-temperature engineering and are termed as engineering ceramics. Al^{3+} can enter the silicon nitride crystal without changing the structure by replacing Si^{4+}, if at the same time N^{3+} is replaced by O[26].

Similar to the compound N_2O_3, a solution was named "SiAlON". SiAlON-ceramics are a specialized class of high temperature refractory materials with high strength (including at high temperature), good thermal shock resistance by molten non-ferrous metals compared to other refractory materials such as

alumina. A typical use is with handling of molten aluminium. They also are exceptionally corrosion resistant, low thermal expansion and oxidation resistance up to above 1000ºC[7].

Sialons are ceramic alloys based on the element silicon (Si), aluminium (Al), oxygen (O) and nitrogen (N). Sialons exist in three basic forms. Each form is iso-structural with one of the two common forms of Si_3N_4, β and α and with sillicon oxynitride. SiAlON is based upon the atomic arrangement existing in β-Si_3N_4. In this material, Si is substituted by Al with corresponding replacement of N by O. The stacking structure in β -Si_3N_4 is different from β -Si_3N_4 in that the long 'channels' which run through the αstructure are blocked at intervals.

In β-sialons, Si in the tetrahedral structure is replaced by Al with limited substitution of N by O. Valency requirements are satisfied by modifying cations occupying the interstitial holes. In this way cations of yttrium (Y), calcium (Ca), lithium (Li) and neodymium (Nd) for example can be incorporated into the structure. Final form of sialon, O-sialon, is iso-structural with silicon oxynitride (Si_2N_2O). The structure of Si_2N_2O consists of layers of Si_3N_4 rings joined by Si-O-Si bonds. In O-sialon, Al and O are replaced by some Si and N atoms. In sintering of Sialon in liquid phase, some metal oxides like Y_2O_3 or MgO are added to promote their sintering which ultimately go to the grain-boundary of ceramics called as oxynitride glass[5,15].

Sialon has the applications in engineering ceramics viz. cutting tool, bearing balls, bearing casing, turbine materials etc[26]. β -Sialons can be considered as a solid solution between Si_3N_4 and Al_3O_3N[12]. Self-propagating high temperature synthesis (SHS) of Sialon is another beautiful method involving high temperature processing[24]. In a separate approach, sialon was synthesized under low n-pressure by gel mixture[24]. Effect of alumino silicates on the pressure less densification of a ceramic with composition in the Sialon region was studied[12]. Self-propagating high temperature synthesis (SHS) was adopted and outstanding characterization was achieved[24].

Densification of silicon nitride based ceramic requires the presence of a transient liquid from which the ß-silicon nitride grain precipitate. It is a common practice as sintering aids ytrrium oxide for magnesium oxide either alone or in conjunction with alumina to the starting α- silicon nitride in order to form eutectics liquid during densification which produces on cooling intergranular glassy phases that are similar in composition to oxynitride glass X-SiAlON where X is equal to Y, Mg, Ca, Si etc.

Material and Methods

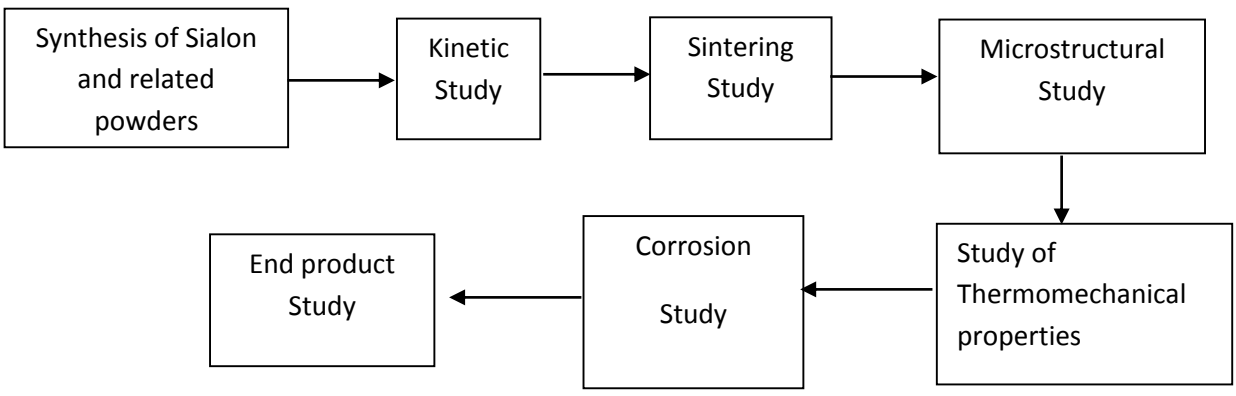
First powders of different varities of oxynitride and related ceramics of various compositions are prepared through different routes from the raw materials and fabricated into different refractory shapes for various engineering applications. Different physical and chemical properties are then measured. The total procedure may be depicted through the flow-sheet:

The synthesis of sialon powders may be achieved by two routes:

a) From the batch materials viz., Si_3N_4, AlN, Al_2O_3 and meatal oxide, SiO_2 (Quartz, Optical Grade) additives of specific particle size. From the batch materials e.g. Si_3N_4, AIN, Al_2O_3 of specific particle size, the powders with some pre-determined composition are mixed and fired at temperatures of > 1799ºC for different periods of time under nitrogen atmosphere.

b) In an another procedure, the carbothermal reduction procedure, the natural aluminosilicates like kaolin, silimanite and pyrophillite are taken as the starting materials. Here the firing is done at around 1500-1600ºC under a controlled flow of nitrogen gas. The reaction kinetics is then studied under different operating conditions. The powders thus produced are next characterized by XRD for different phases subjected to particle size analysis[16].

Sintering: Regular-shaped bars are then fabricated from the green compact through isostatic pressing and their green-densities are found out[17]. In the next step, these compacted bars are fired at high temperature under N-atmosphere.



Study of different properties: Density, thermal expansion, strength, fracture toughness, creep, chemical dissolution etc. are determined on this compacted bar.

Results and Discussion

Composition wise these β -Sialon can be considered as a solid solution between Si_3N_4 and Al_3O_3N[12].Out of different methods, in our case we had adopted the high temperature sintering procedure[26].In the liquid phase sintering of silicon nitride, alumina enters into an extended solid solution[13]. Sialon materials can be considered as a solid solution based on the Si_3N_4structure. Based on the composition and viewpoint, these materials can be regarded as solid solution between Si_3N_4 and Al_3O_3N[12]. Self-propagating high temperature synthesis of Sialon is another beautiful method involving high temperature processing. The class of β–sialon compounds varies over the region from Z = 0 to 2.1 with a general formula $Si_{3-z}Al_zO_zN_{4-z}$. The composition of the liquid was chosen such that the reaction between Y_2O_3, AlN and SiO_2would be Si_3N_4 and Y-Al-garnet (YAG) as follows:

$$6Y_2O_3+20AlN+15\ SiO_2 = 5\ Si_3N_4 + 2(Y_2O_3.5Al_2O_3) \quad (1)$$

It was assumed that YAG would remain at the grain-boundaries and be a highly refractory phase (m.p. 1970ºC). On crystallization, it produced beta Si_3N_4 and YAG[16].

The above processes can be expressed through the following reaction sequences[28]:

$$Al_2O_3+4SiO_2+9C+3N_2 \text{----------} \rightarrow Si_4Al_2O_2N_6 + 9CO \quad (2)$$

$$3(Al_2O_3+2\ SiO_2) +15C +5\ N_2 \text{------} \rightarrow 2\ Si_3Al_3O_3N_5+ 15\ CO \quad (3)$$

$$2(Al_2O_3.SiO_2) +6C+2N_2 \text{----------} \rightarrow Si_2Al_4O_4N_4+6CO \quad (4)$$

Sialon has got two fold advantages over Si_3N_4 as under:

1. Easier densification---- due to longer volume of the transient liquid phase during sintering.
2. Lower cost---- due to the use of cheaper raw material Al_2O_3, the cost of the sintering materials being about 40% of the total cost of the finished product.

Alpha-sialon is another promising material discovered later in the same class which is represented by a general formula $M_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$where x,m and n denote the degree of solution; the material is isostructural to alpha Si_3N_4. It requiresa metal oxide in addition to alumina to stabilize the structure.

The high temperature material sialon ($Si_{6-z}Al_zO_zN_{8-z}$) can be synthesized by carbothermic reduction followed by nitridation. There exists a solid solution between Si_3N_4 and Al_2O_3 which is given an acronym 'Sialon'.

Variation of different properties: Due to excellent intrinsic properties like strength, hardness, thermal shock resistance and chemical inertness, particularly under high temperature, corrosive environment and molten metals, the sialon materials and refractories are used in specific aerospace applications and in different zones of different furnaces. Though alumina is widely used under such condition because of its high chemical resistance, it has very poor thermal shock resistance. Zirconia is better in comparison. However, sialon and other related oxynitride ceramic materials can replace them with their improved thermal shock resistance.

The microstructures of the samples quenched from 1450°C were superficially rather similar to those of the same material cooled under normal conditions to room temperature. Closer examination revealed that the majority of the grains had a more rounded morphology. The presence of the intergranular phase was more evident and could be seen directly in the bright-field images without recourse to the techniques of diffuse dark-field imaging, defocus imaging, or lattice fringe imaging' usually required to reveal the intergranular phase which has been shown in fig. 1.

The thickness of the intergranular phase is substantially greater than the l-rim thickness reported by a number of investigators for the same material under normal cooling conditions. Another striking feature was that the thickness of the intergranular phase was not constant but rather varied significantly from one boundary to another[13].

Most important thing of this work is that the microstructure of the hot-pressed silicon nitride material examined is significantly different at 1450°C from that at room temperature, whereas that quenched from 960°C is substantially the same.

The observations that the intergranular phase is thicker, that there is a larger volume fraction of this phase, and that the grains are more rounded in the material quenched from l400°C, are the most direct evidences that the microstructure changes above about 1000°C. This suggests that interpretations of high-temperature properties in terms of the microstructure evaluated using slowly cooled samples may be misleading.

Conclusion

Sialon of various compositions with the help of excess silica with nitrogen rich liquid shows expected property dependence. On the average for all sintered samples, the theoretical density was almost reached. The properties like fired density and their variation with N-content and % linear shrinkage are well in accordance which have been properly explained. Change of fired density and % linear shrinkage both depend on the sintering temperature and at % N which is the essence of this study.

Thus it can be considered as the simultaneous effect of soaking temperature and presence of nitrogen which are responsible for their variations in our study.

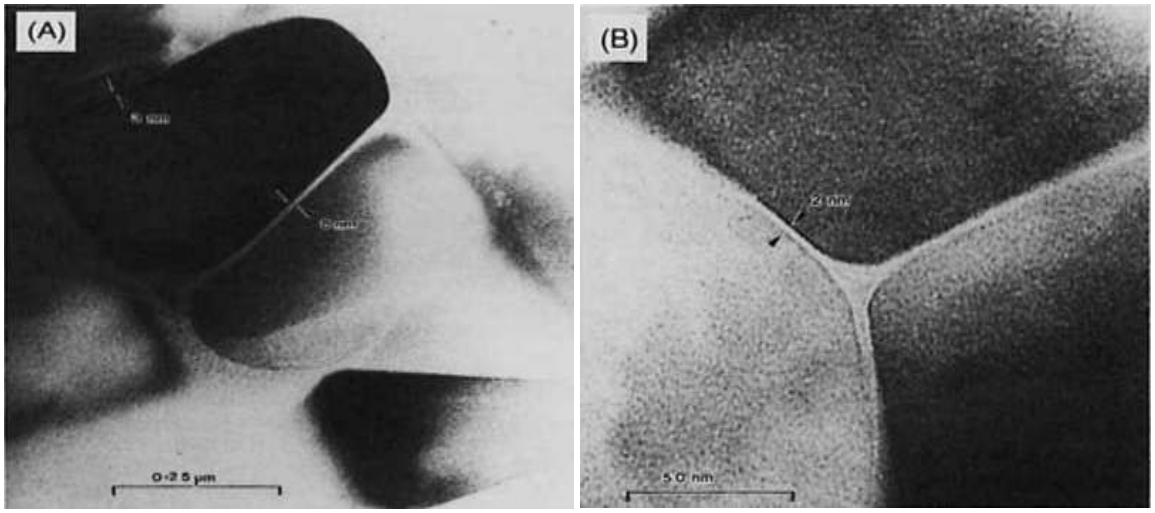


Figure 1: Transmission electron micrographs illustrating the presence of intergranular films (A) 3 and 8 nm in thickness, and (B) 2 nm in thickness in another sample of NC-132 quenched from 1450°C. The intergranular phase is in these bright-field images without having to resort to the microscope techniques normally necessary to image the thinner films characteristic of samples slow- cooled to room temperature[13].

β-sialon reacts with externally added liquid in the system by picking up Al and O, thereby shifting its composition to the higher Z value with concurrent precipitation of $YSiO_2N$ phase from the nitrogen-rich liquid. The later phase increases as the amount of liquid in the starting composition increases. The ambient fracture toughness value is one of the highest published. The value is relatively unchanged to 1200°C after a slight initial decrease at 800°C for a composition with about 5 wt% liquid. The room-temperature strength value is retained to1000°C and deteriorates thereafter.

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