New Application Area for Nitride Based Ceramics as Optical Materials

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Abstract. This study is focused on the production of translucent nitride based ceramics changing different parameters such as additive, starting powder size and sintering conditions. Therefore, two different processes were followed in this research. In first one translucent SiAlON ceramics were improved by controlling specific parameters which were mentioned above. In the second stage, translucent Si\textsubscript{3}N\textsubscript{4} ceramic was obtained also the controlling same parameters. This is a very important result for aerospace and defence industry applications due to these materials high temperature resistivity and mechanical properties.

1. Introduction

One of the most required properties in engineering ceramics is good mechanical properties at high temperature applications. Therefore, SiAlON ceramics are preferred because of the most attractive high-temperature properties. It is a good candidate for high temperature application due to its unique characteristics, such as high hardness and the potential of cleaning the grain boundary phase. However, the application areas of SiAlON ceramics which are very interested with high temperature resistance and mechanical properties are limited with structural applications. On the contrary, it will be an important contribution expanding the use of the functional application area of this material, which has excellent features for defence industry applications which are of great importance today [1, 2]. Many research works have been carried out for transparent/translucent oxide ceramic. Most of the oxide ceramics like Y\textsubscript{2}O\textsubscript{3} and YAG are transparent due to their cubic crystal structure and have no birefringence [3]. However, unlike SiAlON ceramics, these oxide ceramics degrades their properties in severe conditions. There is always a demand for a transparent/translucent material that can resist extreme conditions. New technologies need optical materials with the best mechanical properties. Therefore, in recent years, researchers have paid more attention to developing functional application area for SiAlON ceramics. There are some studies related to the effect of starting raw materials and sintering process on the production of transparent SiAlON ceramics. Transparent ceramics for armour, hard coating and IR window/dome applications should have superior mechanical and thermal properties. Therefore, nitride ceramics have attracted much attention, especially for this kind of application since the 1980s. Kuramoto et al. report that it was possible to produce translucent AlN polycrystalline ceramics in 1989 [4]. Cheng et al. attempt to improve optical properties...
of aluminium nitride ceramics using a microwave sintering process [5]. As well as aluminium nitride, silicon nitride and boron nitride ceramics optical properties have also been investigated by various research groups. SiAlONs are solid solutions of Si$_3$N$_4$ and Al$_2$O$_3$, which are also a well-known class of structural ceramics. Due to the substitution of Si by Al, with a corresponding atomic replacement of N by O, SiAlON production is easy by liquid phase sintering. These materials, generally preferred due to its high temperature stability and mechanical resistivity in structural application areas. However, improving in defence and aerospace industry also required some new materials which have high temperature resistivity, high mechanical and friction properties also optically properties in functional application areas. Therefore, starting in this point translucent SiAlON ceramics researched were started in 1981 by Mitomo et.al [6]. In 1999, Mandal, et al. showed that translucent $\alpha$-SiAlON ceramics doped with Nd$_3$O$_5$-CaO, Nd$_3$O$_6$, CeO$_2$-CaO and Nd$_2$O$_3$-Yb$_2$O$_3$ can be obtained and its properties were improved by heat treatment at 1450°C [7].

SiAlON ceramic is a solid solution and it has different types of phases in its structure such as; $\alpha$-SiAlON, $\beta$-SiAlON, grain boundary phases and porosity etc. All these phases have an import role in the transparency of materials. It was also showed that all different types of phases have an important effect on $\alpha$/$\beta$-SiAlON ceramics. As the amount of these phases increases, the translucency of SiAlON materials worsens. At this point, the refractive index differences emerge. It is known that SiAlON has higher refractive index (2) than Al$_2$O$_3$ (1.76) and YAG (1.84) materials. Therefore, increasing of secondary phase such as alpha or beta SiAlON or grain boundary phase is not requested in this process. However, this is not easy in SiAlON ceramic sintering. From this point, decreasing grain boundary and increasing translucency is the first aim of this research.

In the present study, two different research were carried out. In first one, it was investigated that all effects of sintering, dopants and particle size parameters on optical properties of SiAlONs. In the second one, similar researches were also carried out for Si$_3$N$_4$ ceramics. Si$_3$N$_4$ material is an alternative candidate to nitride based optical materials. Their processing is not much common as an optical materials production and application in literature due to the sintering process difficulty of this material. In practice, sintering of silicon nitride based ceramics is a challenge due to the covalent bond between N and Si atoms. Furthermore, a difference in refractive index between grains and grain boundaries must be minimized in order to obtain a transparent polycrystalline ceramic. To overcome these problems Eu$_2$O$_3$ is used as a sintering additive to promote densification of Si$_3$N$_4$ ceramics and improve optical properties where they dissolve in the solid solution with the main phase. In this research, process controlling was helped to improve translucent Si$_3$N$_4$ ceramic production.

2. Experimental Procedure

2.1. Composition and powder preparation of SiAlON ceramic

Two different $\alpha$-SiAlON compositions were prepared using the following starting powders: $\alpha$-Si$_3$N$_4$ (UBE-10, containing 1.6% oxygen); AlN (Tokuyama, containing 1% oxygen); Al$_2$O$_3$ (99.99%, AKP50); Dy$_2$O$_3$ and Y$_2$O$_3$ (99.99% HC Starck). Samples were doped with single and dual cation and they were called as D, Y and DY, respectively. To investigate the effect of particle size, Dy$^{3+}$- doped composition was milled by Pulverisette 6 Fritsch, Germany in isopropanol alcohol and the sample was named as D$_{10}$. The solvent ratios were determined as given in our earlier research [8-10].

2.2. Sintering process and densification of SiAlON ceramic

Sintering of samples was carried out by gas pressure sintering process at 1850–1900°C under a gas pressure of 100 bars for a 2 h holding time. The entire process was performed in N$_2$ atmosphere. Surface grinding processes were applied to the sintered products in order to thin out the samples down to the desired thickness and to improve the surface quality.
3. Results and Discussion

3.1. Effect of dopant and starting powder size on translucent properties of SiAlONs

It is well known that type of dopant stability is an important effect on grain boundary formation of SiAlON ceramics. In beta-SiAlON ceramic structure, stabilization of dopants is not possible due to its structure whereas this can be tolerated in alpha-SiAlON. Therefore, it is important to selection of suitable atoms which can be stabilized in alpha-SiAlON structure. On the other side, the second important parameter is the amount of liquid phase. SiAlON ceramics can be sintered via liquid phase sintering method and it required enough amount of liquid phase for the process. This liquid phase can be supplied by dopants such as MgO, Y$_2$O$_3$, rare earth, etc. Therefore, in this researched it was focused on decreasing amount of grain boundary, prevention secondary phase formation and increasing densification in the microstructure of SiAlON ceramics. To reach these aims two different dopants Y$_2$O$_3$ and Dy$_2$O$_3$ were used as a single or dual cation in SiAlON compositions. After sintering process of these samples, it was observed that Dy$_2$O$_3$ or Y$_2$O$_3$-doped samples have lower density than dual cation (Dy/Y-doped) doped sample, 3.29 g/cm$^3$, 3.30 g/cm$^3$ and 3.34 g/cm$^3$ respectively [11]. The main phase was observed as an alpha-SiAlON in all samples whereas some amount of AlN-polytype phase has been seen in Y-doped sample (Fig. 1-2). Their transparency was changed related to their microstructure.

![Microstructure of Y$_2$O$_3$-doped sample at 1900°C.](image)

![Microstructure of Dy/Y-doped sample at 1850°C.](image)

Y$_2$O$_3$-doped sample has more elongated grains and higher amount of glassy phase than other samples. Additionally, it was observed that some amount of AlN-polytype in its structure. All these parameters have not deteriorated the transmittance of the sample which is about 45% (Figure 1.a). Comparing with Y$_2$O$_3$-doped sample, Dy$_2$O$_3$-doped one has higher amount of grain boundary phase whereas its grain size distribution is narrower than that of Y-doped. The transmittance of this sample is about 33% even though has higher amount of grain boundary phase (Figure 1.b). Dual cation doped SiAlON composition (Dy/Y-doped) were prepared to increase stabilization of Dy-cation in alpha-SiAlON structure and decrease the amount of grain boundary phase to improve transparency. As it is seen from microstructure, grain size growth was observed whereas the grain boundary phase was still higher than Y-doped one. Therefore, its transmittance is decreased to 25%.

In this point, increasing of the amount of dopant would result with higher amount of grain boundary in samples. Therefore, a novel process was applied to the system to increase density whereas decrease grain boundary phase in the structure of samples. To reach this aim, composition D$_{i0}$ was prepared by milling high energy ball milling system. The powder size of composition was decreased to 137.9 nm from 263.6 nm. This progress was resulted with lowering sintering temperature and decreasing grain boundary phase as it is seen in Fig. 2. Even though decreasing starting powder size the amount of grain boundary phase was not much reduced, as we reported in our previous studies [12]. Additionally, grains were formed in elongated morphology which negatively effects transparency of the sample. On the other
hand, the amount of AlN-polytype was reduced by decreasing powder size. This result has a positive effect on the transmittance percentage of sample as 35%.

Figure 2. a Microstructure of Dy$_2$O$_3$-doped sample at 1850°C.

Figure 2. b Microstructure of D$_{0\theta}$ sample at 1850°C.

3.2. An alternative material to SiAlON

Structure of SiAlON materials is very complicated and its composition stability is not much easy. Therefore, sintered Si$_3$N$_4$ has a much attraction as an alternative optical material for SiAlON. However, there is no more research in this area. In this research the effect of dopant and sintering process was investigated for Si$_3$N$_4$ ceramic materials. Sintering of these materials was carried out by spark plasma sintering. The sintering additives and relative density of Si$_3$N$_4$ ceramics are given in Table 1.

Table 1. Sintering additives and density of samples.

| Sample     | Type of dopant | Density (g/cm$^3$) |
|------------|----------------|--------------------|
| Eu-S@LT    | Eu$_2$O$_3$    | 3.09               |
| Eu-S@HT    | Eu$_2$O$_3$    | 3.29               |

Results showed that sintering conditions have an important role in densification and transparency of the sample. The results were given in figure 3a and b. As it is seen in Figure 3a, the microstructure of Eu-S@LT has a very high amount of porosity and low density. Its theoretical density is about 88%. Therefore, transparency of this sample could not be observed due to porosity and low densification. This is related with lower sintering temperature of samples. Eu-S@HT sample was prepared with the same amount of Eu$_2$O$_3$. This sample was sintered about 55°C higher than the first one. This result showed that without changing type and amount of additive higher densification can be obtained by sintering at higher temperature. This sample reached 94 % density, as 3.29 g/cm$^3$. This result was also supported by microstructural analyses result of sample (Fig. 3b). Even though both samples have alpha and beta-Si$_3$N$_4$ phases, their amount has an important role related with sintering temperature. Alpha-Si$_3$N$_4$ phase shows low temperature stability whereas beta-Si$_3$N$_4$ is stable at higher temperature. Therefore, alpha-Si$_3$N$_4$ phase transforms to beta phase above 1500-1650°C. This temperature range is not constant for all systems, it changeable with amount of grain boundary phase in its structure. All these parameters, such as the amount of alpha and/or beta-Si$_3$N$_4$, porosity and microstructure have an important role on transparency of Si$_3$N$_4$ material. This prior study showed that if sample has high densification microstructure, the amount of grain boundary phase positively affects the translucent properties of samples.
Figure 3.a Microstructure of Eu-S sample sintered at low temperature

Figure 3.b Microstructure of Eu-S sample sintered at high temperature.

4. Conclusion

All results showed that sintering conditions and type of additive have an important role on microstructural and optical properties on nitride based materials. Reducing particle size of starting powder is one of the dominant factors to determine the final morphology and phase assemblage of the nitride based ceramics. Doping SiAlON structure with Dy$^{3+}$ and Y$^{3+}$ also improves the IR transmission. Additionally, this research showed that it is also possible to gained optical property to Si$_3$N$_4$ which is a strong candidate as translucent polycrystalline ceramic for military applications.

5. References

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