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Microwave Reaction Sintering of α-β-Sialon Composite Ceramics

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Abstract

Rapid heating and sintering velocity caused by internal and volumetric heating using microwave energy have potential in uniformly heating and sintering samples and obtaining higher density and finer microstructure. α-β-Sialon ceramics with nominal composition $\alpha:\beta = 20:80$ can be sintered close to TD within 10 min of soaking time in a single mode cavity microwave sintering system operating at 2·45 GHz and higher density, finer grain size and good mechanical properties are obtained also. © 1996 Elsevier Science Limited. All rights reserved.

1 Introduction

Recently many new phases have been found during research on the multi-phase diagram of Si_3N_4-based ceramics and many solid solution sialon materials such as high-hardness, good thermal shock resistance α-sialon and high flexure strength, high fracture toughness β-sialon ceramics have been fabricated. The phase diagram and microstructural characteristics of the sialon system also show that the compatibility relationship of α-sialon and β-sialon provides a avenue for design of composite sialon materials and one of the most promising approaches to reinforce and toughen Si_3N_4-based ceramics through in-situ growth of elongated or platelet-like grains in their microstructures.[1] A thorough study of the phase relationships of the Y, Si, Al, O, N system (Fig. 1.) made clear that α-sialon and β-sialon were compatible in their phase relationships, thus making it possible to obtain proper composition design with optimum properties which single-phase ceramics cannot provide. Moreover, some additives such as Y_2O_3 can be accommodated into the lattice of α-sialon, thus decreasing the content of glassy phases and leading to improved high temperature mechanical properties.[2] At present, most reported high density sialon ceramics, usually have been obtained by hot pressing[3] or high temperature sintering under high nitrogen gas pressure;[4] with conventional pressureless sintering it is difficult to achieve complete densification.

Microwave sintering of ceramics is a new rapidly developed technology having the potential for overcoming problems encountered in conventional processes. It offers the possibility to produce a unique microstructure and improved properties because of fundamental differences between microwave and conventional heating. The use of microwave energy in performing high temperature chemical reactions for the synthesis of ceramics materials also offers many advantages over conventional methods. Ahmad and Clark[5] showed that in the zinc oxide and alumina system, the formation of $ZnAlO_4$ was more rapid in a microwave field and the increase in reaction rates suggested an enhanced diffusion mechanism. Also microwave heating appeared to increase coefficients in the sintering of alumina[6] and create higher excitation levels to increase chemical and physical reactions by making reaction away from the equilibrium state.[7] It was determined that the reaction times for synthesis of some ceramic materials can be reduced by as much as three orders of magnitude using microwave heating technology.[8] In this study, we describe microwave reaction sintering behavior, microstructural features and some mechanical properties of α-β-sialon ceramics.

2 Experimental Procedure

2.1 Composition design

Figure 2 shows the compatible tetrahedron of α-sialon-β-Si_3N_4-β-sialon-YAG. We can see from Fig. 2 that α-sialon ($m = 1$, $n = 1{\cdot}7$) containing the highest oxygen content is compatible with β-sialon (from β_0 to β_{10}). The material was designed (with nominal composition of $\alpha:\beta = 20:80$) based on the phase relationship of the compatible tetrahedron. The starting powders used were Si_3N_4, AlN, Al_2O_3, Y_2O_3. The properties of Si_3N_4 and AlN powders are listed in Table 1. Al_2O_3 and Y_2O_3 were 99·9% pure. The oxygen contents of silicon nitride and aluminum nitride powders were taken into account into computing the composition.

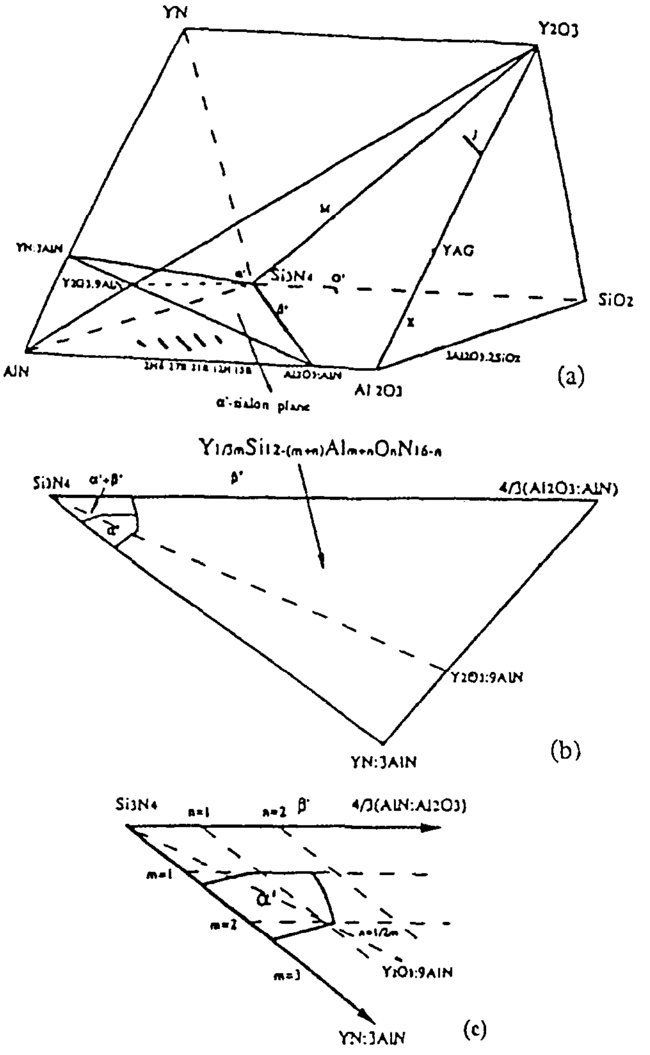

Fig. 1. (a) A section of α-sialon plane in Y-sialon system, showing coexistence of α- and β-sialon phases, (b) α-sialon plane, (c) an enlarged corner of α-sialon plane.

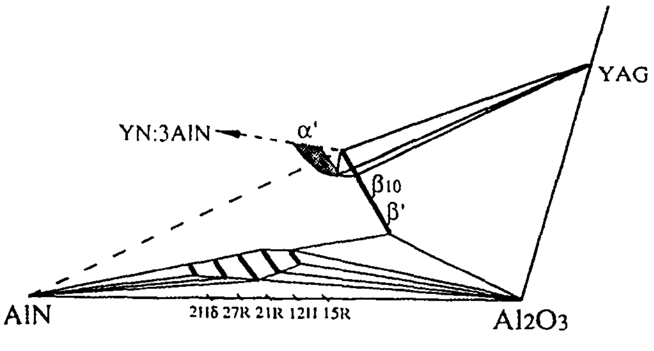

Fig. 2. Compatible tetrahedron of α-sialon-β-Si_3N_4-β-Sialon-YAG.

Table 1. Properties of Si_3N_4 and AlN powders

	N	*O*	*C*	*d*(*μm*)
α-Si_3N_4	38·09 wt%	1·01 wt%	—	0·35–0·45
AlN	32·5 wt%	0·94 wt%	0·42 wt%	10·4

2.2 Forming shape and sintering

The mixtures of powders were ball-milled (using sialon ball) in absolute alcohol for 24 h. After drying and sieving, the powder mixtures were die-pressed into bars, and then isostatically pressed under a pressure of 200 MPa. The microwave reaction sintering experiments were carried out in a nitrogen gas flow in the insulation configuration shown in Fig. 3 in a single mode applicator microwave sintering system operating at 2·45 GHz. Sintering temperature was 1650°C with holding time of 5–10 min.

2.3 Measurement

Density and linear shrinkage rate of the samples were measured at several predetermined temperatures. Densities were measured by the water immersion methods and surface temperatures were measured by an optical pyrometer. The phase compositions of specimens were determined by X-ray diffraction. Their microstructures were observed by HREM, TEM and SEM techniques. Hardness was measured by hardness equipment [AKASHI(AVK-A)] and flexural strength was determined by the three-point method with a cross-head speed of 0·5 mm/min. Fracture toughness was determined by the indention method using a load of 10 kg.

3 Results and Discussion

3.1 Microwave reaction sintering behavior of α-β-sialon

Pure silicon nitride-based ceramics are poor couplers and relatively transparent to microwave

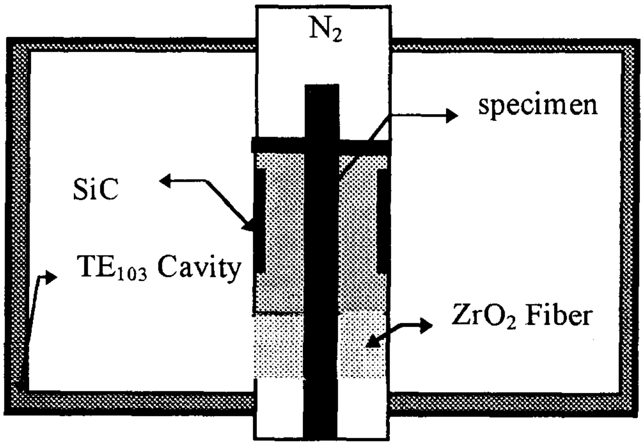

Fig. 3. Insulation configuration used in microwave reaction sintering of α-β-sialon.

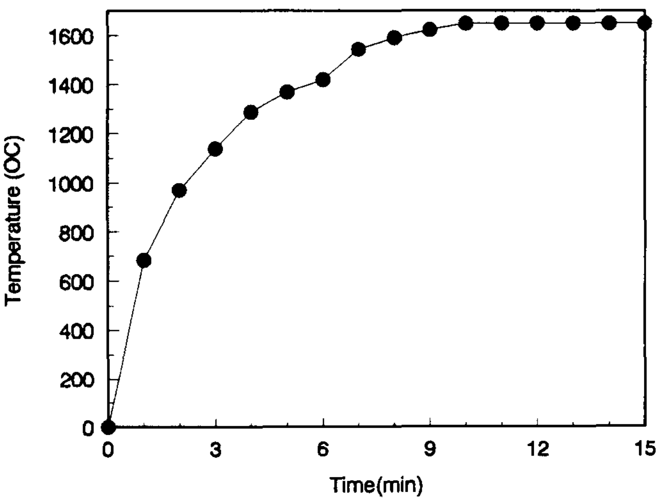

Fig. 4. The curve of measured surface temperature dependence on time.

energy at room temperature because of their low dielectric loss, and thus are very difficult to heat by themselves. The insulation configuration shown in Fig. 3 has to be used to reach high sintering temperature. Usually two measures were adopted during the microwave heating of low dielectric loss materials:

1. Addition of high loss materials to low loss materials to help low loss materials to absorb microwave energy, often limited because of changing basic properties of low loss materials;
2. Using high loss materials to surround low loss materials to achieve conventional and microwave hybrid heating.

In our study, we adopted the second method by using the excellent absorption ability of SiC ceramics at room temperature to heat the specimen rapidly to sintering temperature. The packing powder is made up of SiC+Si_3N_4+BN+AlN and it serves many functions: helps the specimen absorb microwave energy well, prevents decomposition of Si_3N_4 and AlN and uniformly heats the specimen etc. Figure 4 shows the curve of measured surface temperature dependence on time. The whole heating cycle can be potentially divided into three stages: rapid heating (0–1400°C), unstable heating (1400–1650°C) and stable heating (1650°C). During rapid heating, the specimens are heated for 4 min at a constant input power of 400–500 W. A temperature of 1400°C can be quickly reached. Then unstable heating begins until sintering temperature is reached. The unstable heating stage is critical to the whole sintering cycle. Careful tuning and strict input power control are a must to avoid cracking and arcing during this stage. Because dielectric loss of the whole heated system (including SiC, packing powder and the specimen) varies little with temperature, correct maximal input power equates to correct maximal temperature reached as shown in Fig. 5. Thermal runaway phenomena and other factors which cause the specimen crack, arc and inability to heat can be avoided by application of appropriate insulation configuration and careful input power control. This also can be attributed to the nature of microwave heating. As a result of internal and volumetric heating of microwave energy, thermal stresses may be significantly reduced due to a reduced intergranular temperature gradient from that seen in the conventional heating. Thus, microwave heating makes possible the heating of large and irregular shape ceramics with freedom from cracking.

Figure 6 shows the curve of relative density vs sintering temperature. With increasing sintering temperature, relative density increases accordingly. Densification occurs evidently between 1300 and 1650°C and relative density is 96·2%TD at

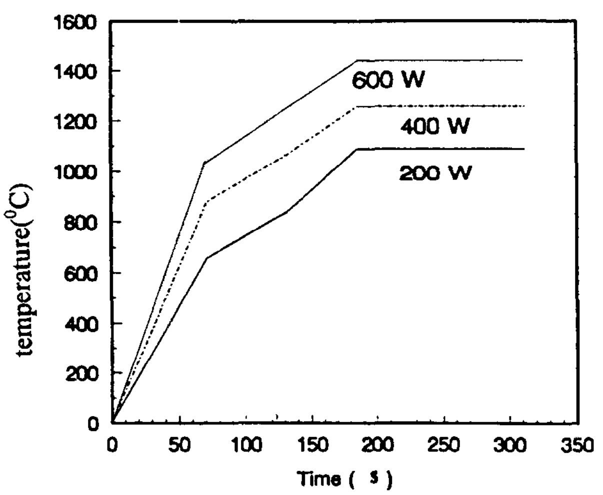

Fig. 5. The maximal achieved temperature vs different input power in microwave reaction sintering of sialon.

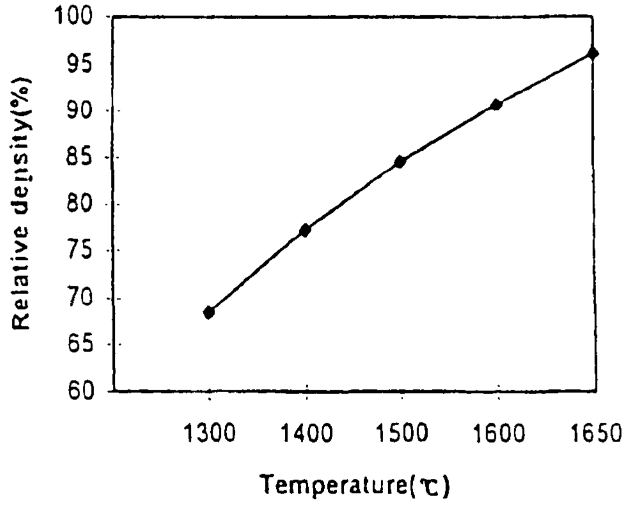

Fig. 6. The curve of relative density vs sintering temperature in microwave reaction sintering.

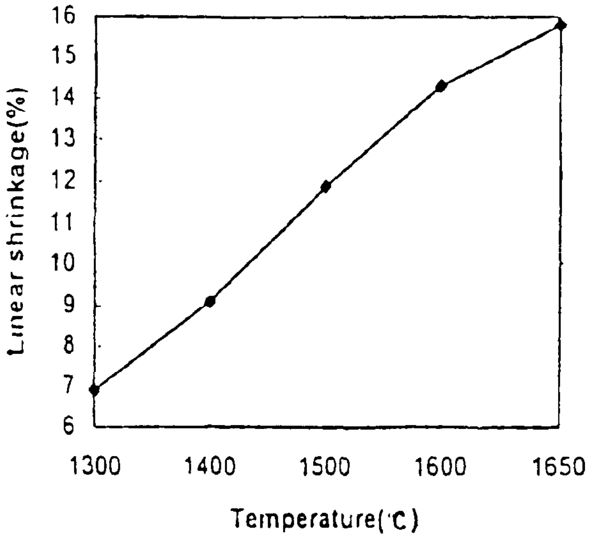

Fig. 7. The curve of linear shrinkage vs sintering temperature in microwave reaction sintering.

temperature of 1650°C. At 1650°C, relative density increases with soaking time and reaches the maximal value (99·2%TD) at a holding time of 10 min, almost equal to TD. It is very evident that microwave reaction sintered sample densifies very rapidly with relatively low measured temperature and short time. Enhanced sintering behavior over conventional heating is evident and may be attributed to enhanced diffusion in the microwave field. Recent literature[9,10] reported that microwave heating can lower the sintering temperature of some materials and greatly shorten sintering time. There is a view that 'microwave effect' which was not found in conventional heating caused improved properties and enhanced sintering. The mechanisms are not yet well understood and explained.

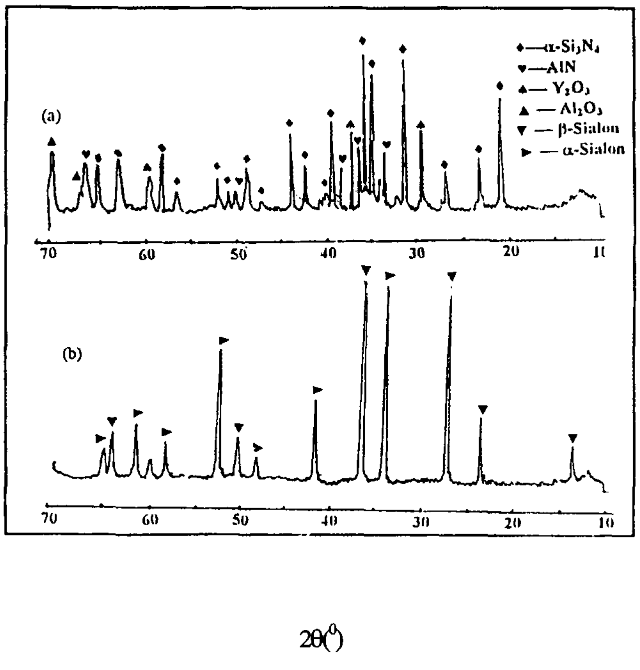

Fig. 8. XRD pattern (a) before reaction sintering; (b) after reaction sintering.

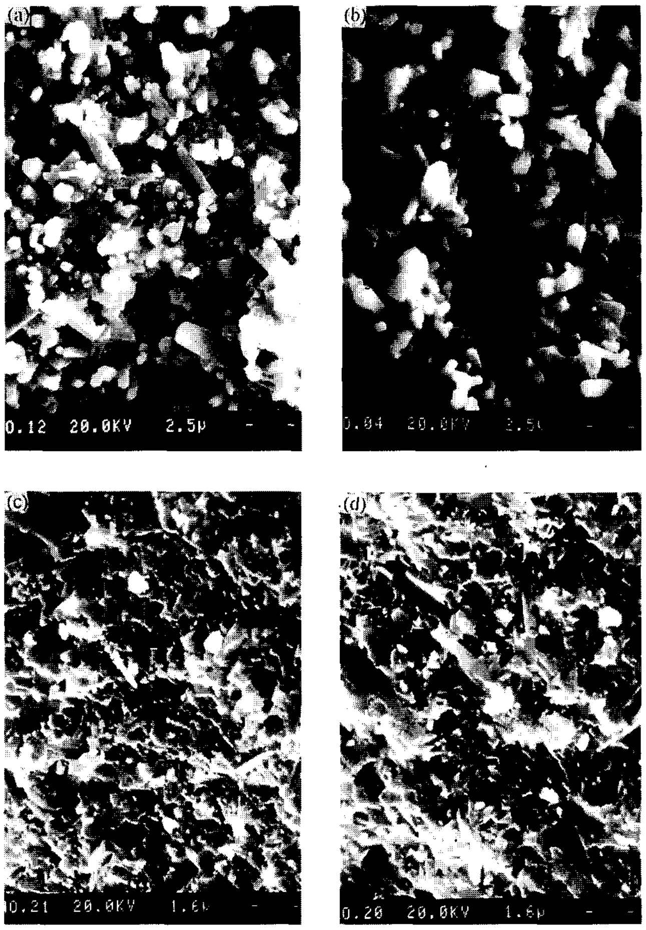

Fig. 9. SEM micrographs of microwave reaction sintering α-β-sialon ceramics (a) natural surface with 5 min soaking time; (b) natural surface with 10 min soaking time; (c) fracture surface with 5 min soaking time; (d) fracture surface with 10 min soaking time.

Some reports[9,11] on the microwave processing of ceramics suggested that enhanced transport properties occurred in an electromagnetic field. Also, microwave rapid heating led to the early activation of grain-boundary and lattice diffusion before surface diffusion could significantly coarsen the microstructure and decrease the driving force for sintering. Figure 7 shows the relationship of linear shrinkage vs sintering temperature. We already know that a liquid phase sintering mechanism is responsible for densification of α-β-sialon ceramics. At 1300°C, linear shrinkage is 6·9%; at 1650°C, linear shrinkage reached the highest value of 15·8%, and at the same time density of the specimen is 96·2%TD, showing that a liquid phase has already formed at a surface temperature of 1300°C while the liquid phase area exists at the corner of SiO_2 with minimum formed temperature of 1350°C,[12] it is possible that microwave heating lowers sintering temperature.

3.2 Phase composition and microstructure

Figure 8 shows the XRD pattern (a) before microwave reaction sintering and (b) after microwave

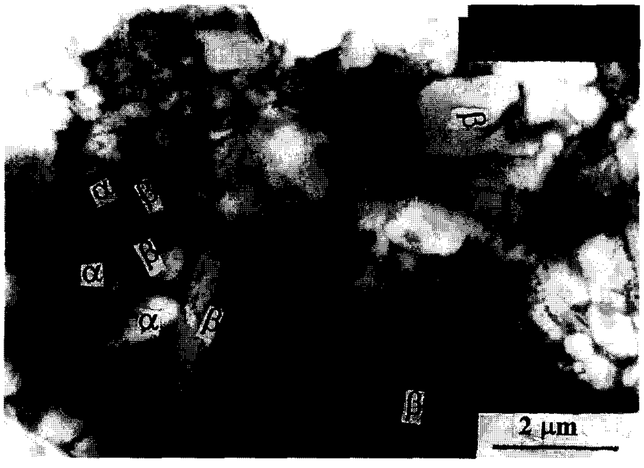

Fig. 10. TEM micrograph of α-sialon-β-sialon multiphase materials.

reaction sintering. The occurrence of reaction is evident from the virtual disappearance of all diffraction peaks related to the reactants. XRD analysis shows that the only crystalline phase in the samples are α and β-Sialon, and the intergranular phase exists in the glassy state. Also from the XRD pattern we can know that β-Sialon is the major phase after reaction sintering, which coincides with the initial composition design. Brook[13,14] proposed that rapid heating led to improved microstructure and high density with the development of finer and more uniform grain structures by a rapid transition to higher temperature which caused a suppression of surface diffusion and other coarsening without densification mechanisms that exist at lower temperature, while application of high heating rates in conventional heating was limited by slow heat conduction and thermal shock. Figure 9 shows SEM micrographs of natural surface and fracture surface of microwave reaction sintered samples after 5 and 10 min. From these micrographs we can see that the grain is fine and elongated grains of β-Sialon have formed; equiaxed α-sialon grain is evident also.

Fig. 11. TEM micrograph showing glassy phase between α-sialon-β-sialon grains.

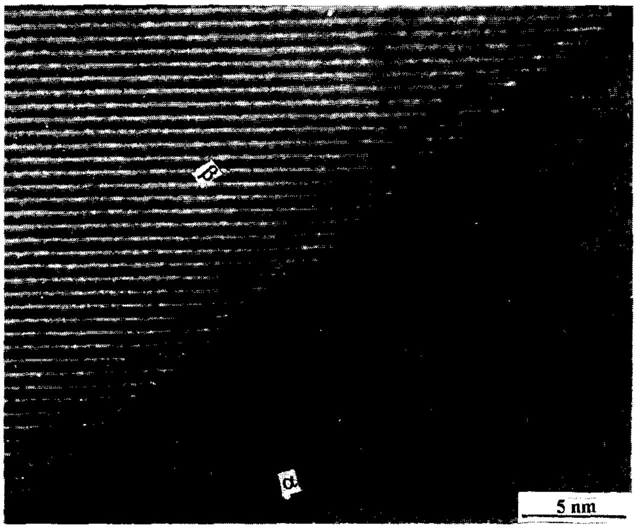

Fig. 12. HREM micrograph of a grain boundary of α-β-sialon.

From SEM micrographs of natural and fracture surfaces, the specimens with soaking times of 5 min and 10 min all have completely densified and no observed gas pore exists in the whole fracture surface. The grain microstructure of the specimen with holding time of 10 min is more uniform than that of the specimen with holding time of 5 min. Moreover, fracture methods both have transgranular and intergrain fracture which are signs of high strength materials. This result coincides with results of our mechanical properties. It is evident that microwave heating obtains uniform microstructure and improved mechanical properties at relatively low temperatures and short times, difficult to achieve in conventional heating.

Figure 10 shows a typical TEM micrograph of microwave reaction sintered α-β-multiphase sialon. Crystalline phases and the amorphous grain boundary phase can be clearly identified by their different contrast. β-sialon grains are generally elongated in shape while α-sialon grains show equiaxed morphology. Glassy phases are concentrated mainly in the pockets formed between the β-sialon grains and α-sialon grains as shown in Fig. 11, or triple points of major crystalline phase.

Figure 12 shows HREM micrograph of a grain boundary between α and β grains; β phase is viewed along the (100) plane while α grain is viewed along the (101) plane. The width of the grain boundary is very small, signifying a very clean grain boundary. A grain boundary between two β grains of different orientations is also shown in Fig. 13. It can be observed that liquid phase penetrated into the grain boundary to a depth of 1–2 nm.

3.3 Mechanical properties

Mechanical properties of sintered samples are listed in Table 2. Values obtained cannot show the

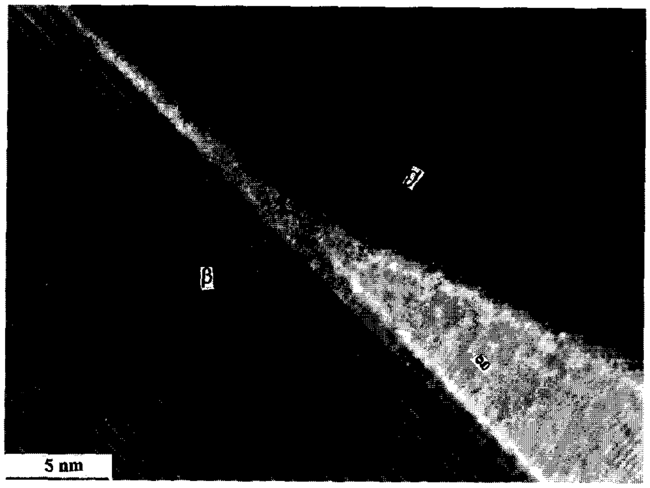

Fig. 13. A grain boundary between β grains of different orientations.

Table 2. Mechanical properties of microwave reaction sintered α-β-sialon composite ceramics.

Specimen	*Sintering temperature (°C)*	*Holding time (min)*	HR_A	*Flexure strength (MPa)*	*Fracture toughness* ($MPa\,m^{1/2}$)
1	1650°C	5	91·7	454·8	5·8
2	1650°C	10	92·4	544·1	6·3

real mechanical properties of the specimen because of the limitations of the microwave heating cavity. The sintering cavity is too small to accommodate the whole sample, so the sample must be sintered by continuous movement from the top to the bottom, thus unavoidably causing non-uniform sintering. Efforts are now directed to get true estimate of mechanical properties and with some improvements we will be able to uniformly sinter the whole large specimen to obtain better mechanical properties.

From Table 2, the mechanical properties of the specimen with a holding time of 10 min are better than those of the specimen with a holding time of 5 min. This can be attributed to higher density and more uniform microstructure of the former.

4 Conclusion

Using proper insulation configuration, α-β-sialon composite ceramics with nominal composition design $\alpha:\beta = 20:80$ can be successfully microwave reaction sintered to close to TD at 1650°C with a holding time of 5–10 min in a single mode applicator microwave sintering system operating at 2·45 GHz. Uniform microstructure and good mechanical properties are obtained also.

Acknowledgements

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