

Spark Plasma Sintering of Heat-treated Nicalon SiC Fibre Reinforced β -sialon Ceramics

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Abstract

Spark Plasma sintering of Nicalon SiC fibre reinforced β -sialon Ceramics was carried out so that tough ceramic matrix composites were able to produce. Even though Sialon ceramics is one of the toughest ceramic compared with other engineering ceramics, they still need to be reinforcement. Therefore, in this study, sialon matrices were reinforced with sort Nicalon SiC fibres. Before reinforcement, the matrix densification temperature were lowered with different oxide additives and the fibre surface and physical properties were changed so that fibre withstand sintering conditions and become compatible with the sialon matrix and under mechanical forces. For that purpose, the SiC fibre were heat treated blow 45 bar CO atmosphere. As a result of heat treatment both fibres tensile strength were increased and a self-coating was achieved. On the other hand, low temperature densification of sialon ceramics was also achieved with different densification additives. Finally spark plasma sintering of short heat-treated SiC fibre reinforced β -sialon ceramics were carried out with SPS and SEM microscopy and X-ray analyses were performed. The result showed that toughening of sialon matrix with SiC fibres was successful.

Keywords: Nicalon, SiC fibres, heat-treatment, sialon ceramics, reinforcement, silicon nitride

1.Introduction

Toughening of ceramic matrix composites (CMCs) depends upon the ability of reinforcing fibres to arrest crack propagation. It can be imagine that the presence of high-strength fibres, which are well bonded to the matrix, might also greatly improve strength. However, what is more urgently required is increase in toughness. This depends upon mechanisms of energy absorption such as fibre deponding and frictional pull-out, and a balance must be achieved between load transfer across the fibre/matrix interface and fibre debonding and slip in the region of the propagating crack [1]. Therefore, the mechanical performances of CMCs are very sensitive to the properties of the fibre/matrix interface.

Silicon nitride (Si_3N_4) materials present good thermal, mechanical and tribological properties, which enable them to sustain the wearing conditions enduring some engineering parts, such as valves in diesel engines, ball bearings, sealing rings or tools for metal cutting and shaping. The densification of these materials commonly requires the use of alpha- Si_3N_4 powders with oxides additives and high temperatures in the range of 1700–1800°C leading to the liquid-phase sintering. The liquid-phase sintering includes particle re-arrangement, solution-precipitation and elimination of closed porosity. When Pressureless sintering or hot pressing are employed, α to β phase transformation and grain growth jointly occur during Si_3N_4 densification. Sialon ceramics are the silicon nitride based ceramics and obtained substitution of Si with Al and N with O during high temperature liquid phase sintering. They have been developed mainly during the last four decades, and densification and transformation studies still continue in different ways. Much of the improvement in mechanical properties of sialon ceramics has been the result of the careful control of Si_3N_4 starting powder quality, processing and subsequent consolidation [2-4].

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Although β -sialon has found many applications in engineering, the range of applications would be enlarged by increasing its toughness by fibre reinforcement. Because of both chemical and thermal compatibility, SiC fibres are the most suitable reinforcement for Si_3N_4 and sialon ceramics. Whilst high-purity SiC fibres can withstand high temperatures, the refractoriness of the oxygen-containing Nicalon fibres is limited and this is why most previous work has focused on their use as reinforcement for glass matrix composites. However, in the present study, the use of CO heat-treated Nicalon fibres has enabled the higher temperatures required for the densification of β -sialon ceramics to be reached without any associated degradation of the fibres, or without fibre-matrix sticking which inhibits pull-out and decreases toughness[5-7].

The spark plasma sintering (SPS), which is a pressure assisted pulsed direct current sintering, is the most employed technique to sinter powders. SPS allows much faster heating rates and shorter sintering times compared to conventional sintering techniques such as pressureless sintering, hot pressing or hot isostatic pressing. SPS technique exceedingly increases the sinterability of most of the materials and allows the possibilities for developing new materials. Up to now, a wide range of materials, from metals to ceramics, including different kinds of composites, as well as functionally graded materials has successfully sintered [8-15].

In this study, the potential of SPS to develop Nicalon SiC fibre reinforced β -sialon ceramics is studied in depth. It has been discussed the possible effect of pulsed direct current on the liquid phase formed during the sintering of the sialon ceramics. Among the numerous SPS mechanisms proposed, there is a general consensus on the important role of both the rapid Joule heating and the intrinsic electric field effects [8-10]. For Sialon materials, Nygren's group[11] proposed a dynamic ripening mechanism to explain the very fast in situ formation of tough interlocking microstructures by SPS annealing dense compacts. Accordingly, the motion of charged species was enhanced by the electric field and rapid heating, which increased diffusion and homogenization in the liquid phase [12-13]. This mechanism may be considered as an enhanced solution-precipitation process involving a rapid grain growth.

In the present work, it has been focused mainly on keeping strength of the reinforcing fibre properties during the densification process of SPSed –heat-treated short SiC fibre containing Si_3N_4 powders with liquid forming oxide additives. As stated above, allows shortening of β -sialon sintering time from hours to minutes, getting total densification with negligible grain growth and/or phase transformation [14-15]. Using a composition with 2 wt.% of MgO and 7 wt.% of Y_2O_3 and 8wt.% Sm_2O_3 as sintering aids , However, when same composition is sintered by HP, temperatures of 1650 °C and holding times of 60 min are required to get full densification.

2.Experimental Procedure

Nicalon SiC fibres, Type NL-207, supplied by Nippon Carbon Japan, were used as the reinforcement after a gas pressure heat-treatment. Silicon nitride LC 10 grade supplied by Starck (Germany) and combinations of the densifying agents; MgO, Y_2O_3 , Al_2O_3 and AlN were used as starting powders for β - SiAlON matrices. This powder composition was ball-milled in isopropanol alcohol, dried and sieved. This sialon composition was cold pressed and CIPed to get pellet. Initially monolithic β -sialon pellets were either hot-pressed or SPSed at 1650°C for ½ hour to observe densification behaviours. The SiC fibres were heat-treated in a gas pressure furnace under 45 bar CO atmospheres to change mechanical and surface properties. These heat-treated fibres were chopped in approximately 0.5-1mm and mixed with

β -sialon starting powders in aqueous environment. The partially dried mixtures were cold-pressed to give pellet and to squeeze out excess water. These pellets were either for hot-pressed and spark plasma sintered. SEM (JEOL- JSM-6060LV) image analysis and XRD (Rikagu) examination were carried out.

3. Results and Discussions

Polymer precursor Nicalon SiC fibres contains SiO_2 and free carbon which reacts together during matrix densification and causes fibre degradation resulting in lower toughness. In order to prevent this fibre degradation, a heat treatment technique was explored in previous studies [6]. According to this technique, the fibre yarn was initially passed through at 500°C to burn out surface organic binder and wrapped in a graphite reel then accommodated in a home-made GPS furnace. At room temperature 20 bar CO gas was filled up and the furnace was run. When the gas pressure furnace temperature went up 1600°C , 45 bar CO pressure was obtained, and the fibres were heat-treated for $\frac{1}{2}$ hour at these conditions. After pressurised CO heat treatment of SiC Nicalon fibres, the fibre properties were totally changed. As a result of chemical reaction during heat-treatment, 6.5 % weight gain observed and the fibre surfaces were coated with in situ reaction product carbon. This unexpected surface coating was a wonderful property change for ceramic matrix composite reinforcement since the coating would provide pull-out under loading. Apart from this in situ surface coating, tensile strength of the Nicalon SiC fibres was surprisingly increased from 2.8 GPa to 4.2 GPa. These property changes were great discovery for ceramic matrix composite production because strong and surface coated fibres can reinforce ceramic matrices better than other fibres.

Even though fibre properties have been developed under high pressure, still care must be taken during hot-press or SPS sintering of heat-treated fibre reinforced β -sialon matrices since both is open atmosphere sintering despite both sample was embedded in BN. In order to avoid fibre degradation, low temperature densification must be provided to keep fibre properties. For this purpose, 2 wt.% MgO, 7% Y_2O_3 and 8wt.% Sm_2O_3 were used as oxide additives. The combination of these additives with surface silica of Si_3N_4 powders reacts at low eutectic temperatures at 1250°C and sealed the fibre air reactions as well as BN encapsulation. Y_2O_3 is the best oxide additives in terms of alpha to β - sialon transformation during hot-pressing or spark plasma sintering. MgO is best for liquid phase sintering and Sm_2O_3 is third oxide component to lower eutectic temperature. If the gained fibre properties can be kept with low temperature during SPS consolidation, it can be reached excellent CMC properties.

Table Comparison of SPSed density and hardness with hot-pressed samples

	Temp. $^\circ\text{C}$	Soaking time min.	Density g/cm^3	Hardness GPa
Hot-pressed monolithic β -sialon	1650	60	3,44	16.95
SPSed monolithic β -sialon	1600	10	3.44	16.80
Hot-pressed β -sialon composites	1650	60	3,18	13.93
SPSed β -sialon composites	1500	10	3.31	15.15

Density hardness measurement and were performed and tabulated in Table 1. As shown in Table 1 the density of SPS monolithic sialon samples remained same (3.44 gcm^{-3}) with hot-pressed sample since both samples were reached theoretical density. Even though both monolithic β -sialon density and hardness (16.80-16.95 GPa) were same, with SPS method SiC fibre reinforced β -sialon composites were produced at lower temperature (1600°C) and shorter sintering time (10 min). These results revealed that sintering with SPS method of

sialon composite could be more successful compared with hot-pressing. For this reason, heat treated fibre were cut and aqueous mixed with β -sialon starting powders containing oxide additives and the compacted green bodies were spark plasma sintered at lower temperatures and times compared with hot-pressing. As a result of lower temperature and shorter SPS sintering, higher density and hardness were achieved. While the density of hot-pressed composite was 3.18 gcm^{-3} and hardness was 13,93 GPa, SPSed sample was $3,31 \text{ gcm}^{-3}$ and 15,15 GPa respectively. This was great success in terms of fibre property stability during sintering. Fibre degradation can be prevented with and sort low temperature sintering. Hence, It can be expressed that SPS is much more effective sintering method than hot-pressing.

X-ray diffraction and EDS analysis were also carried out for the spark plasma sintered SiC fibre reinforced β -sialon composites. The XRD result in Fig.1 showed that majority of phases was alpha silicon nitride. Insufficient α to β -sialon transformation was took place. However, in spite of 10 minutes sintering time, significant amount of transformation was occurred.

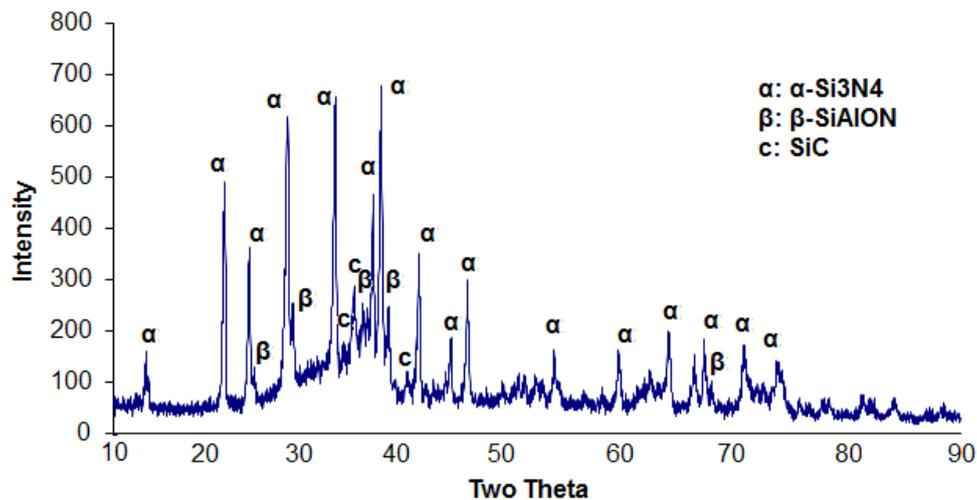


Fig.1 X-ray analysis of SPS sintered β -sialon composite

EDS analysis of fibre matrix was taken during SEM examination (Fig.2a) and given in Fig.2b and Fig.3. The EDS result of matrix showed that the structure was consisted of Si, Al, O, N elements for β -sialon $z=1$ and Si_3N_4 and Y, Sm, Mg elements for oxide additives. These findings proved that the matrix was combination of β -sialon $z=1$ ceramics, α - Si_3N_4 ceramics and grain boundary glass which was necessary for solution-precipitation mechanism.

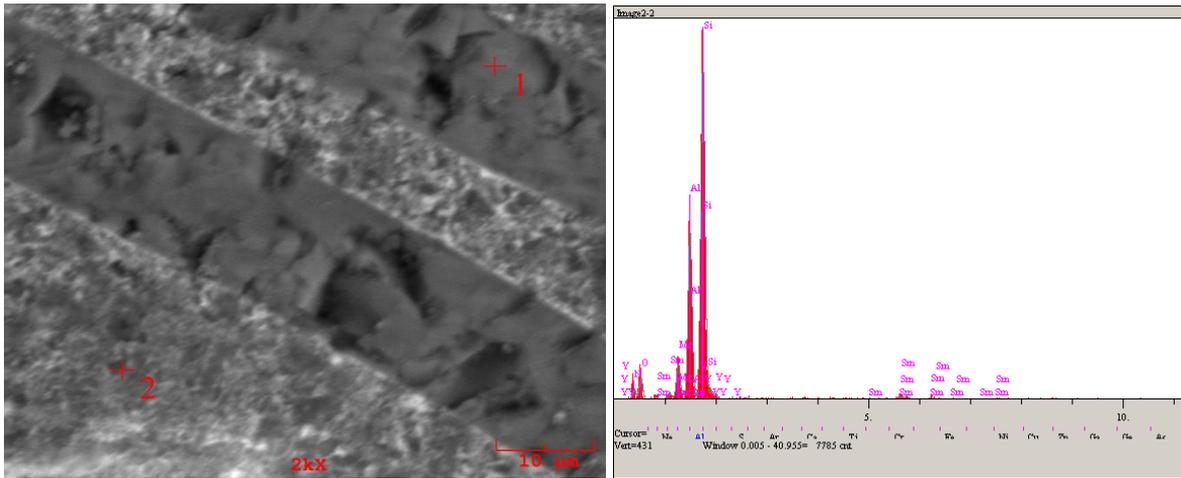


Fig.2 EDS analysis of β -sialon matrix and Nicalon SiC fibres a) EDS points in SEM image b) matrix EDS result

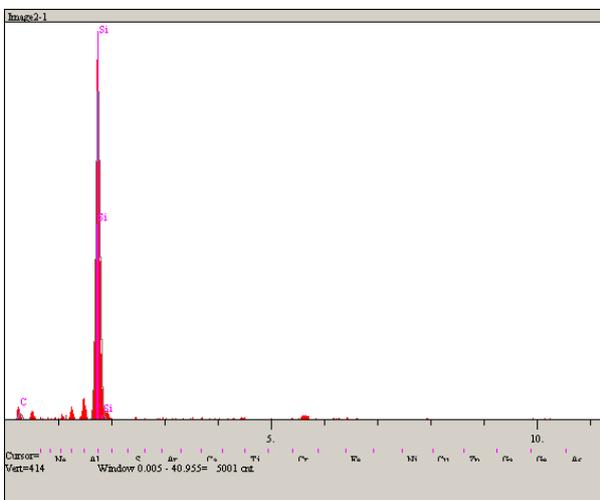


Fig.3 EDS results of SiC fibres

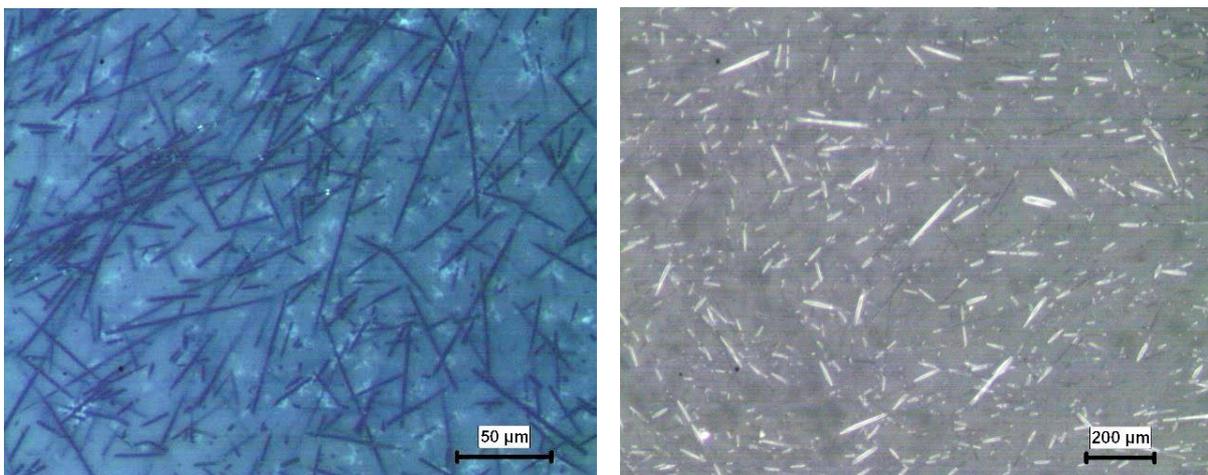


Fig.4 Stereo microscope of β -sialon composites a) background distribution b) polished surface

Stereo microscope of SiC fibre reinforced β -sialon composites are shown in Fig.4.a-b. As shown in Fig.4., homogeneous fibre distribution was obtained, and fibre orientation was not observed. Fig 4.a shows 3D background fibre distribution as well as surface distribution. This provides isotropic property for β -sialon ceramic composite. Continuous fibre reinforced ceramic composites give well properties in along the fibres, but worse properties across the fibres. Short fibre reinforcement of β -sialon composites increased flexural strength and toughness of sialon matrices in each direction.

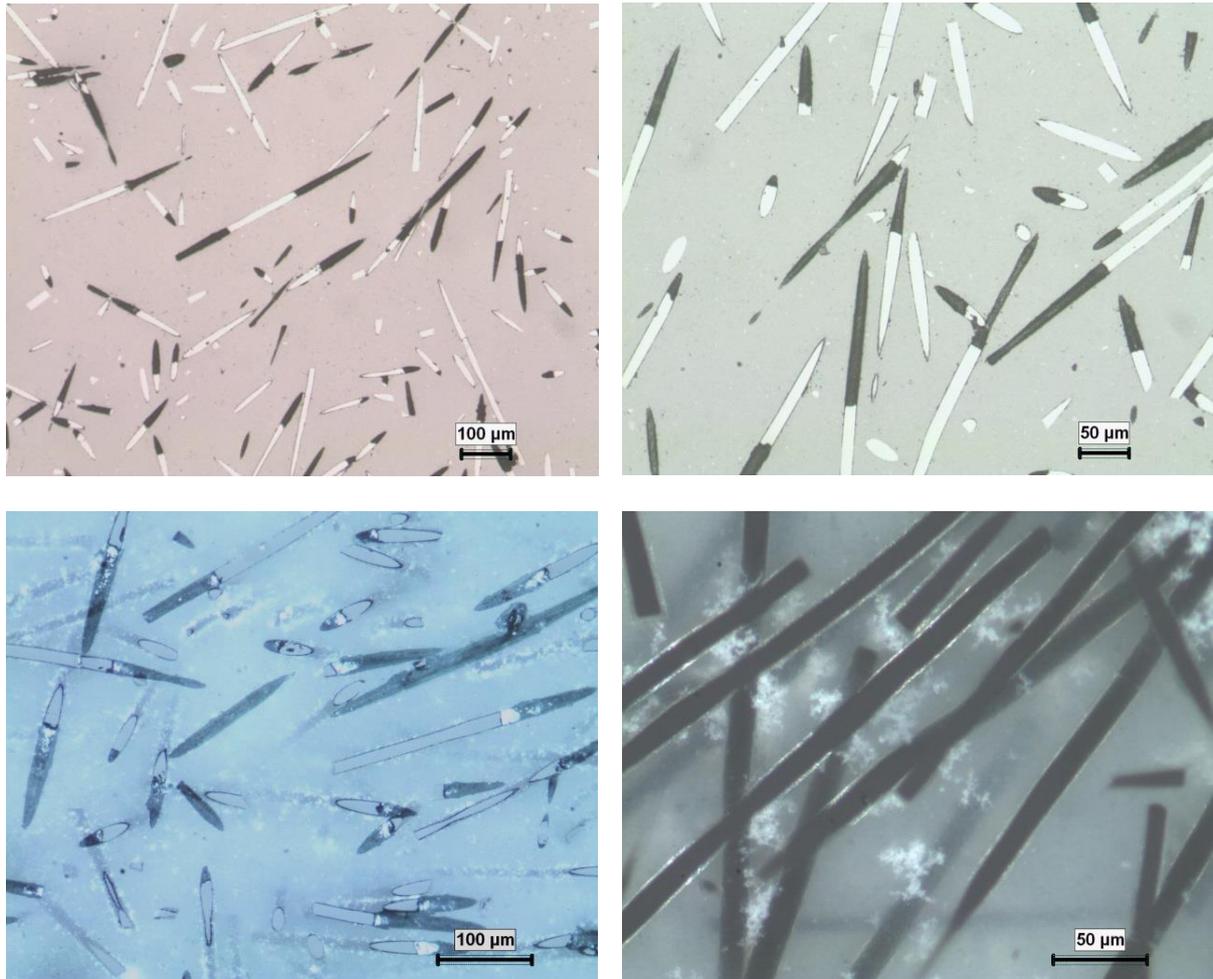


Fig.5 Optical micrograph of SiC reinforced β -Sialon composites a-b) surface distribution c-d surface and background distribution (fibre coating is visible)

In order to examine fibre degradation and fibre coating, high magnification of optical micrographs was selected as shown in Fig.5. As shown in Fig.5, no significant fibre degradation during SPS sintering was observed. Homogeneous and non-oriented fibre distributions were obtained within β -sialon ceramics as result of short fibre reinforcement. As result of heat treatment of the fibres, they were self-coated and the strength of the fibres was increased. In optical micrograph, this gives contrast and leads the fibre coating visible. As shown in Fig.5 b,c,d, between fibres and matrices there are thin lines which are represents in situ fibre coating. This coating can help crack deflection and fibre pull-out and prevent catastrophic fracture under loads. By this means, the applied load is transferred from matrix to

the fibres and reinforcement is achieved. If the mechanical and physical properties are protected, significant strength increases are shown resulting β -composites.

4. Conclusion

Spark plasma sintering of heat treated discontinuous SiC fibre reinforced β -sialon $z=1$ composites has been able to produce. The SPS sintering conditions were the lower temperatures and shorter durations compared with hot-pressing conditions. With SPS sintering, density and hardness of the composite were increased by means of fast densification and transformation. For β -sialon transformation, SPS time was enough to complete transformation. To complete transformation, longer duration should be used. The fibre properties were preserved during SPS. The coating of the fibres was remained within the composites and no surface reactions were observed.

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