Microstructural investigation of $\alpha$/$\beta$ SiAlON/SiC composites by analytical transmission electron microscopy

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1. Introduction

Recently, many studies have been made to develop the application field of SiAlON-based ceramics. $^{[1,2]}$ Owing to their finely changeable mechanical, thermal and optical properties, these materials have been successfully used so far in a wide range of applications such as cutting tools, ball bearings and light emitting diodes (LEDs). $^{[2]}$ The incorporation of particulate second phase into ceramic matrixes could be used as a reinforcement agent to obtain the enhanced properties of resulting composite material. $^{[3]}$ Herein, the composites thus prepared are designed for specific purposes. In this approach, generally speaking, the main properties are the composites thus prepared are designed for specific purposes. In this approach, generally speaking, the main properties are the microstructure is of major interest for understanding the specific properties of composite material.

The incorporation of SiC particles into $\alpha$/$\beta$ SiAlON matrix leads to an enhancement on the properties. The precise detection of SiC particles in the microstructure is therefore of major interest for understanding the nature of resulting material. Here, $\alpha$/$\beta$ SiAlON/SiC composite was analytically examined by using transmission electron microscopy (TEM). Considering the results, nano-sized spherical SiC grains were visualised to be encapsulated with $\alpha$/$\beta$ SiAlON matrix. A decisive contrast between the $\alpha$/$\beta$ SiAlON and SiC phases was not observed by conventional (C)TEM. However, the SiC grains, $\alpha$/$\beta$ SiAlON matrix and grain boundary/intergranular phases were easily able to distinguished to each other via C-K (284 eV), N-K (401 eV) and O-K (532 eV) edges in energy filtering (EF)TEM 3-window elemental mapping and scanning (S)TEM-spectrum imaging (SI)-electron energy loss spectroscopy (EELS) analyses. It is anticipated that analytical (A)TEM approach presented here helps the precise determination of different reinforcement particles and matrix phases in many kind of composite systems.

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CaO was used in order to avoid $\alpha \rightarrow \beta$ SiAlON transformation, $Y_2O_3$ to increase the stability and hardness of $\alpha$-SiAlION and $Sm_2O_3$ to form elongated $\beta$-SiAlION grains and hence enhance the fracture toughness.\(^{25,26}\) The spray dried granules were uniaxially pressed to pellet forms. Afterwards, the cylindrical tablets were sintered at 1940°C for 1 h under 22 bar nitrogen atmosphere using the gas pressure sintering (GPS) method.

The densities of sintered pellets were measured by Archimedes’ principle. Phase identification and $x$ to $\beta$% ratio\(^{27}\) for SiAlON phases were performed using X-ray diffraction (XRD, RINT-2000, Rigaku Co., Japan) analysis, operating at 40 kV and 30 mA using Cu-K$\alpha$ radiation ($\lambda = 1.5406 \text{ Å}$). The data were collected by continuous scan mode at the 2$\theta$ range from 18 to 45° with a step size of 0.02° and scanning speed 0.5°/min. The general microstructural observations from the surface of sintered sample, which was prepared by mechanically grinding and polishing routes, were conducted using a field emission gun (FEG) SEM (Zeiss Supra 50 VP), working at 30 kV accelerating voltage under variable pressure (VP) without coating.

For ATEM investigations, an electron transparent specimen was prepared by conventional mechanical polishing and Ar-ion beam thinning (Leica Microsystems EM RES101). Afterwards, the sample was characterized by using a field emission TEM (Jeol 2100F), operating at 200 kV and equipped with a high angle annular dark field scanning transmission electron microscope (HAADF-STEM) detector (Fischione), annular dark field (ADF) and bright field (BF) STEM detectors (Gatan STEM pack), an energy filter and parallel electron energy loss spectrometer (EELS, Gatan GIF Tridiem). In STEM-based spectrum imaging (SI) and EELS analyses, an electron spot with 1–2 nm in diameter was used. Furthermore, a drift corrector was performed to avoid any possible drifts that may occur at nano-scale during the acquisition of STEM-SI analysis. In order to acquire EELS spectra and maps, the convergence and collection semi-angles were used as 9.2 and 15.7 mrad, respectively. The spectrometer

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**Fig. 1.** Laser diffraction particle size analysis of commercial $\alpha$-SiC starting powder.

**Fig. 2.** (a–d) Secondary electron (SE) SEM images at different magnifications revealing the morphological characteristics of commercial $\alpha$-SiC starting powder.
energy dispersion was also chosen in 0.2 and 0.5 eV/channels. The backgrounds in EELS and energy filtering transmission electron microscope (EFTEM) 3-window elemental mapping analyses were subtracted according to power-law.28)

3. Results and discussion

Density measurements showed that sintered pellets were almost fully dense (99.7%). The XRD pattern following sintering was given in Fig. 3. Herein, it was found that the starting powders were mainly converted to α-SiAlON, β-SiAlON and SiC phases. The α/β SiAlON ratio was calculated as 22/78. A very small amount of grain boundary melilite phase (Mi = Ln2Si3−xAlxO3+xN4−x; Ln: Y, Sm and Ca) including sintering additives was also detected.26)

The general microstructural features of α-β SiAlON/SiC composite, which was acquired by backscattered electron (BSE) imaging, were seen in Fig. 4. At a first glance, highly elongated rod-like β-SiAlON grains and bright intergranular phases could be easily distinguished as dark and white contrast, respectively. In addition to this, near-equiaxed shape α-SiAlON grains with grey contrast due to the incorporation of sintering additives, i.e. Y, Sm and Ca, into the lattice structure26),29) could be seen in the microstructure. Also, spherical-shaped nano-sized particles (marked with red coloured arrows in Fig. 4) showing the nearly same contrast with β-SiAlON phase was observed to be generally dispersed onto the β-SiAlON grains. These are suggested to be SiC phases owing to their small sizes with respect to α-SiAlON grains.29)

In order to precisely determine the microstructure evolution of α-β SiAlON/SiC material after sintering, BF-TEM images in Figs. 5(a)–5(d) were firstly obtained from the different regions of the α-β SiAlON/SiC composite. Here, as similar to SEM results (Fig. 4), the most surprising observation was that spherical-shaped probable SiC grains with approximately 50–250 nm in diameter were encapsulated with α-β SiAlON matrix phases, as shown by black coloured arrows (Fig. 5). This type of formations was also defined as inclusions or small cores in β-SiAlON grains, enhancing the mechanical properties, especially bending strength, of matrix phase.22),23) Besides, a well bonding and dense structure between the α-β SiAlON matrix and intergranular triple junction phases was clearly observed.

Secondly, STEM imaging routes were conducted to distinguish the possible SiC phases within the microstructure. STEM images in Figs. 6(a)–6(d) also confirmed the first results showing the availability of nano-sized probable SiC grains (marked with blue arrows in Fig. 6) in the α-β SiAlON/SiC composite.26)

![Fig. 3. The XRD pattern of α-β SiAlON–SiC composite [The metallic Si was used as internal standard. Here, β, α and M' correspond to beta-SiAlON, alpha-SiAlON and melilite (Ln2Si3−xAlxO3+xN4−x) phases, respectively].](image)

![Fig. 4. BSE-SEM image of α-β SiAlON–SiC composite following gas pressure sintering. Please note that the highlighted red arrows show the probable SiC particles.](image)

![Fig. 5. (a–d) BF-TEM images acquired from the different regions of α-β SiAlON–SiC composite.](image)

![Fig. 6. (a–c) Z-contrast STEM-HAADF, (b–d) STEM-BF images of α-β SiAlON–SiC composite.](image)
diffraction condition. Hence, the scope, the more crystalline this phase is under the imaging mode, the brighter a phase appears under the micro-
or number (Z), which means that regions containing higher atomic elements would appear brighter in the microstructure. Therefore, in the Z-contrast HAADF-STEM images [Figs. 6(a) and 6(c)], the \(\alpha-\beta\) SiAlON matrix consisting of lower Z elements could be visualised as almost black whereas intergranular phases with higher Z elements, i.e. Ca (20), Y (39) and Sm (62), could be seen as white regions in contrast to the BF-TEM images given in Fig. 5. However, a distinct and sharp contrast between the \(\alpha-\beta\) SiAlON and SiC phases were not detected, since there is a difference only one atomic number between the C (Z = 6) and N (Z = 7) elements. Moreover, as a special case in HAADF-STEM imaging mode, the brighter a phase appears under the microscope, the more crystalline this phase is under the specified diffraction condition. Hence, \(\alpha-\beta\) SiAlON grains in the Z-contrast HAADF-STEM images [Figs. 6(a) and 6(c)] might be indeed SiC phases, and vice versa.

Additionally, STEM-BF images as a complementary visualisation route were given in Figs. 6(b) and 6(d). Please note that especially the contrasts of \(\alpha-\beta\) SiAlON matrix and intergranular phases were similar to that of BF-TEM images shown in Fig. 5 and were different that of Z-contrast images in Figs. 6(a) and 6(c). The reason was simply that the STEM-BF images, as like in the BF-TEM, were interference patterns, and image contrast was depended on the relative phases of the transmitted or diffracted beams. Therefore, the probable SiC grains encapsulated by \(\alpha-\beta\) SiAlON matrix could be more visible in STEM-BF images [Figs. 6(b) and 6(d)].

In order to chemically clarify the existence and distribution of SiC phases in \(\alpha-\beta\) SiAlON matrix, energy filtering TEM (EFTEM) 3-window elemental mapping analysis was performed to the \(\alpha-\beta\) SiAlON/SiC composite, and the results were demonstrated in Fig. 7(a)–7(f). Here, to obtain the high signal to background ratios, the Si-L\(_2,3\) (99 eV), C-K (284 eV), N-K (401 eV) and O-K (532 eV) edges were intentionally chosen for the EFTEM-3 window elemental maps [Figs. 7(b)–7(e)]. Based on the EFTEM elemental map results [Figs. 7(a)–7(f)], the enhanced contrast with respect to BF-TEM images [Figs. 5(a)–5(d)] was seen in zero-loss EFTEM image [Fig. 7(a)]. Here, the spherical nano-sized probable SiC grains were more clearly observed to locate on the elongated \(\beta\)-SiAlON grain. Considering together the results of Si-L and C-K edges EFTEM-3 window elemental maps [Figs. 7(b) and 7(c)], the SiC grains could be easily seen on the rod-like \(\beta\)-SiAlON grains. Furthermore, considering Figs. 7(b) and 7(c) in detail (please see the white coloured arrows), nano-sized SiC phases were found as trapped grains on the \(\alpha-\beta\) SiAlON matrix. More surprisingly, the big-sized SiC particles, almost as large as SiAlON grains, were also detected between the intergranular and \(\alpha-\beta\) SiAlON phases [shown in circle in Figs. 7(b) and 7(c)]. This gives important data about the coalescence of the individual SiC grains during the sintering. Similar observations were also made by Yurdakul et al. through EFTEM-3 window elemental mapping technique for in-situ formation of nano and big-sized SiC grains, arising from the intensive reactions between TiCN and \(\alpha-\beta\) SiAlON phases. In view of the findings of N-K and O-K edges EFTEM-3 window elemental maps [Figs. 7(d) and 7(e)], it was observed that nitrogen (N) signals were highly concentrated on the \(\alpha-\beta\) SiAlON matrix whereas oxygen (O) signals were intensely acquired from the grain boundary thin films and intergranular phases. Please also note that almost no N-K and O-K signals were observed in SiC phase regions on the Figs. 7(d) and 7(e). At this point, it could be deduced that the SiC grains, \(\alpha-\beta\) SiAlON matrix and grain boundary thin films/intergranular phases were successfully distinguished to each other in the microstructure by using C-K, N-K and O-K edges, respectively [Fig. 7(f)].

In STEM spectrum imaging, converged electron probe is systematically moved along the sample at nanometre scale and the resulting signals are collected. Unlike traditional mapping, the total spectrum is stored at each point allowing advanced spectral processing to be performed for every pixel in the spectrum image with high spatial resolution. Therefore, in order to confirm the EFTEM-3 window elemental mapping results [Figs. 7(a)–7(f)], STEM-SI data set was first collected from the electron transparent \(\alpha-\beta\) SiAlON/SiC sample, given in Figs. 8(a) and 8(b). Z-contrast STEM image [Fig. 8(a)] showed the square spectrum.
image area along with the selected spatial drift correction rectangular and the last position of electron beam after acquisition was completed. The view of spectrum imaging (SI) in STEM mode (Every pixel herein contains the chemical information), (c–e) qualitative EELS elemental maps of C-K (284 eV), N-K (401 eV) and O-K (532 eV) edges, respectively, and (f) RGB (RedGreenBlue) composite map.

Fig. 9. (a) Z-contrast STEM image showing where electron probe was focused during EELS analysis (red coloured dot), (b–d) EELS spectra acquired from triple junction (TJ) phase shown in Fig. 9(a). Please note that chemical composition of TJ consists of Y–Sm–Ca–Si–Al–O–N elements.

In order to see the Y–Sm–Ca sintering additives’ distribution within the microstructure after sintering, the EELS analysis in STEM mode was carried out. Figures 9(b)–9(d) shows the EELS chemical analysis results acquired from the triple junction (TJ) phase, which was marked with red coloured dot in Fig. 9(a). Based on the EELS data [Figs. 9(b)–9(d)], it can be seen that the chemical composition of TJ consists of Y–Sm–Ca–Si–Al–O–N elements. This clearly reveals that sintering additives (Y–Sm–Ca) locate in amorphous and/or crystalline triple junction secondary phases, reported in a previous study.26)

4. Conclusions

In this study, the microstructure investigation of α-β SiAlON/SiC composite was characterised by ATEM techniques. Based on the results, composite microstructure was consisted of α-β SiAlON matrix, SiC grains and intergranular grain boundary phases. Nano SiC grains were also visualised to be encapsulated with α-β SiAlON matrix. Although CTEM imaging methods revealed the general microstructure features of α-β SiAlON/SiC composite, a decisive contrast between the α-β SiAlON and SiC phases herein was not observed. However, using analytical EFTEM 3-window elemental mapping and STEM-SI-EELS analyses; the SiC grains, α-β SiAlON matrix and grain boundary thin films/intergranular phases were distinguished to each other through C-K (284 eV), N-K (401 eV) and O-K (532 eV) edges. Thus, chemical imaging of individual and coalescent SiC grains in the microstructure could be easily obtained. Considering the results presented here, it is anticipated that concept of ATEM investigations will be also useful model study in order to precisely determine the microstructure evolution for different reinforcement particles and matrix phases in many kind of composite systems.

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References