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Study for the origin of fracture of advanced pore-free silicon carbide with damage tolerance

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It had been well known that the fracture of SiC manufactured by conventional reaction sintering method was caused by one of the pores in that. However, according to the recent studies, pore free SiC so called APF-SiC was developed by improvement of reaction sintering method. As the result, the strength and the damage tolerance ability rise and then the cause of fracture of APF-SiC changed from pores to something else. Therefore we have investigated fracture surface of APF-SiC by using FE-SEM and EDS in order to demonstrate the cause of fracture. As the result, we found the inclusion that consisted of allotropes of Carbon covered with very thin SiO_2 and SiN layer. And the size of the inclusion is ten times larger than that of SiC grain. Considering from present results, the inclusion is the one of the cause of fracture of APF-SiC.

Key-words: Advanced pore-free silicon carbide, FE-SEM, EDS, Inclusion, Allotropes of carbon, Oxide and nitride of silicon

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1. Introduction

Monolithic ceramics have excellent mechanical properties e.g. heat resistance, lightweight and high stiffness. Therefore, they are one of the hopeful engineering materials of today. However, it is difficult to apply monolithic ceramics to the part which is needed the high-reliability. Because the fracture toughness of the monolithic ceramics is lower than metals, namely catastrophic fracture takes place in the monolithic ceramics.

Previously, it was reported that the origin of the fracture of the conventional monolithic ceramics was the pores in that, thus the mechanical properties of the monolithic ceramics depended on the sizes and the distributions of the pores.[1] For example, in the case of the familiar conventional reaction sintering SiC (RS-SiC), the pores exist the grain boundaries and occupy approximately 2 vol% of amount of RS-SiC and then the residual non-reacted Si distributes un-uniformly.[2),3]

Therefore, to reduce the pores and to control the distribution of the residual Si are important to improve mechanical properties of the monolithic ceramics.

Then, the advanced pore-free silicon carbide ceramics (APF-SiC) was developed by new reaction sintering method (details of manufacture process of APF-SiC are mentioned in section 2).[4] APF-SiC scarcely includes the pores. Moreover the residual Si is distributed uniformly along SiC grain boundary in APF-SiC. As the result, the strength of APF-SiC is twice as large as RS-SiC and the damage tolerance ability of that is higher than that of other monolithic ceramics, because the accumulated internal energy is released by the preceding failure of the residual Si grains which is distributed along SiC grain boundaries.[5] These points of APF-SiC are greater than conventional RS-SiC. Thus it can be expected that the mechanism of the fracture of APF-SiC is different from that of RS-SiC. Then, we have investigated the texture and element concentration map of the fracture surface of APF-SiC and then discussed the improvement points of the manufacturing process of APF-SiC.

2. Manufacture process of advanced pore free silicon carbide[4]

Flowchart of manufacture process is shown in **Fig. 1**. At first, SiC powder of grade of over 99.0% with mean size of 1 μm (produced by SHOWA DENKO) and Carbon black (C) powder of grade of over 99.98% with mean size of 0.3 μm (produced by Cancarb Ltd.) were mixed with the water

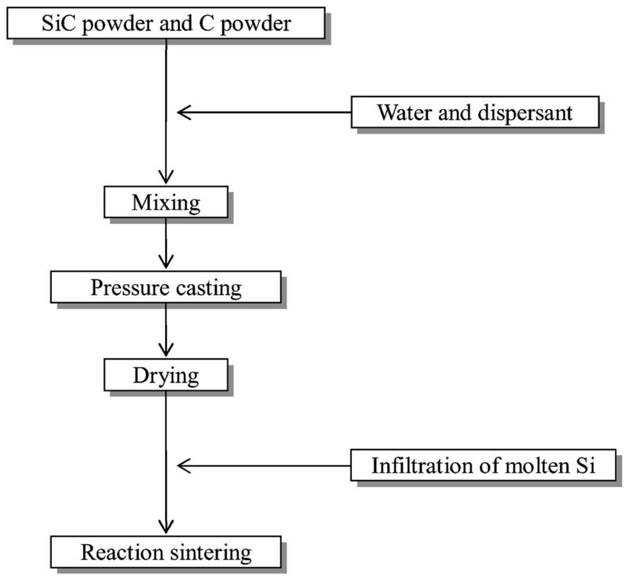

Fig. 1. Flowchart of manufacture process for APF-SiC.

and the dispersant. Subsequently, the mixture was inserted in the ceramics mold and pressed and then dried. After that, this material (SiC/C) was made to react with melting metallic Silicon (Si) powder of grade of over 99% (produced by Kojyundo Chemical Laboratory) in a crucible under the pressure below 1 Pa at the temperature 1700 K.

3. Experimental method

We used APF-SiC mentioned in section 2, namely it was reported in reference[4] as the samples. At first, the samples were ruptured by 4-point bending test method based on JIS R 1601[6] with a crosshead speed of 0.5 mm/min at room temperature using the universal materials testing machine (Autograph, AGS-J, Shimadzu, capacity: 5kN). Subsequently, we observed the fracture surface of the sample by using field emission scanning electron microscopy (FE-SEM) and investigated the chemical composition mapping by energy dispersive spectrum (EDS).

4. Results and discussions

4.1 Observations of fracture surface using FE-SEM

FE-SEM images of the fracture surface of APF-SiC are shown in **Fig. 2**. It is seen that a large inclusion exists in the center of Fig. 2(a). On the other hand, the granular type surface of polycrystalline SiC can be seen on the fracture surface apart from the inclusion. The high magnification image of Fig. 2(a) is shown in Fig. 2(b), the surface of the inclusion are smooth and the edge of the inclusion is obviously bonded with SiC grains. In Fig. 2(c), we show another fracture surface image of APF-SiC. A characteristic dent exists on the fracture surface. Considering from the size of dent, the dent is the impression of an inclusion which is the same type one observed in Fig. 2(a). From these observations, it is demonstrated that some inclusions exist in this material and the sizes of that are very larger than that of SiC grains.

4.2 Composition analysis of fracture surfaces by EDS

An image and its concentration mapping images obtained by EDS measurement of each element of the same fracture surface of APF-SiC are shown in **Fig. 3**. EDS measurement performed at the condition I given in **Table 1**. From the SEM image shown in Fig. 3(a), it is seen that cracks extended in the vicinity of the surface acting maximum stress. This tendency of the fracture surface is similar to that of conventional ceramics such as RS-SiC. The EDS element concentration mapping images of Silicon (Si) and Carbon (C) are shown in Figs. 3 (b) and (c), respectively. It is seen that the element concentration of Si is higher than C in the most of

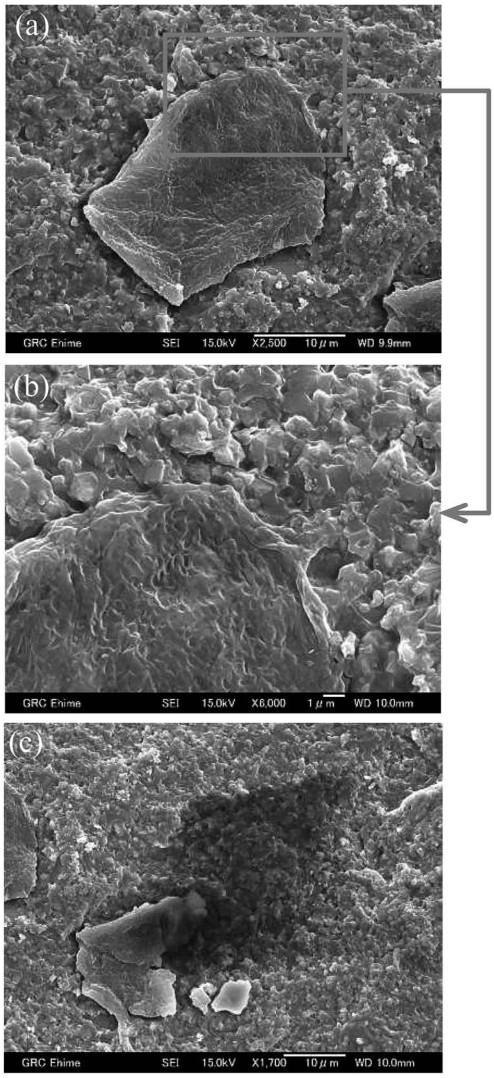

Fig. 2. FE-SEM images of the fracture surface including an inclusion; (a) Fracture surface andinclusion in low magnification, (b) Inclusion in high magnification, (c) Characteristic shape dent.

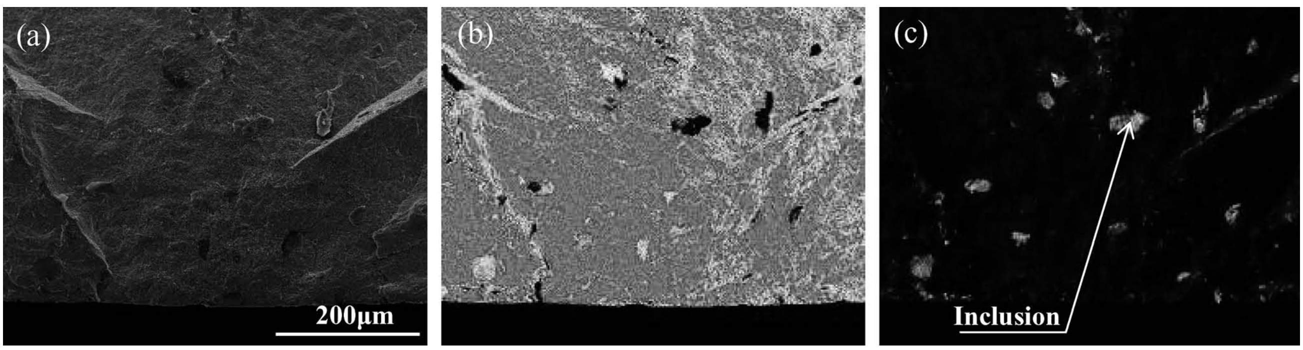

Fig. 3. FE-SEM image and elements distributions from EDS mapping; (a) Fracture origin region, (b)Elements distributions of Si, (c) Elements distributions of C.

the part in the images. This result indicates that the most of part of APF-SiC consists of SiC grains and residual Si. However, in some part of figure, the element concentration of Si is obviously lower than that of C. This result indicates that the masses of C exist in APF-SiC as the inclusions.

In order to obtain the detail information for the inclusion surface, the spot analyses of the inclusion surface was carried out by using EDS at the condition II given in Table 1. The spot analysis locations indicate in the FE-SEM image shown in **Fig. 4** and EDS spectrums obtained from locations ***a***, ***b*** and ***c*** are also shown in Fig. 4. At the point ***a***, Si and C are only detected. On the other hand, Nitrogen (N) and Oxygen (O) are detected with C and Si at the point **b** and **c**. These results indicate that oxides and nitrides are formed around of the inclusion mainly consisted of C. Moreover, to investigate the distributions of N and O on the surface of inclusion, a concentration mapping measurement was performed for the area of the inclusions at measurement condition III given in Table 1. The obtained concentration mapping images are shown in **Fig. 5**. The concentration of C is obviously denser than other elements and that of Si is also

Table 1. Operating Conditions for EDS

Operating condition	I	II	III
Accelerating voltage /keV	15	5	5
Working distance /mm	10	10	10
Specimen tilt /rad	0	0	0
Magnification	×200	×850	×14000

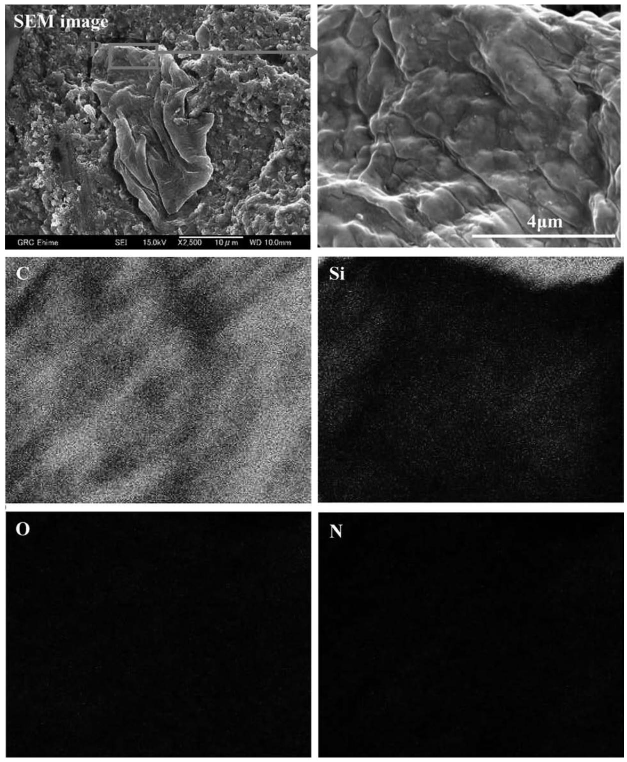

Fig. 5. FE-SEM images and EDS mappings the elements distributions of C, Si, O and N.

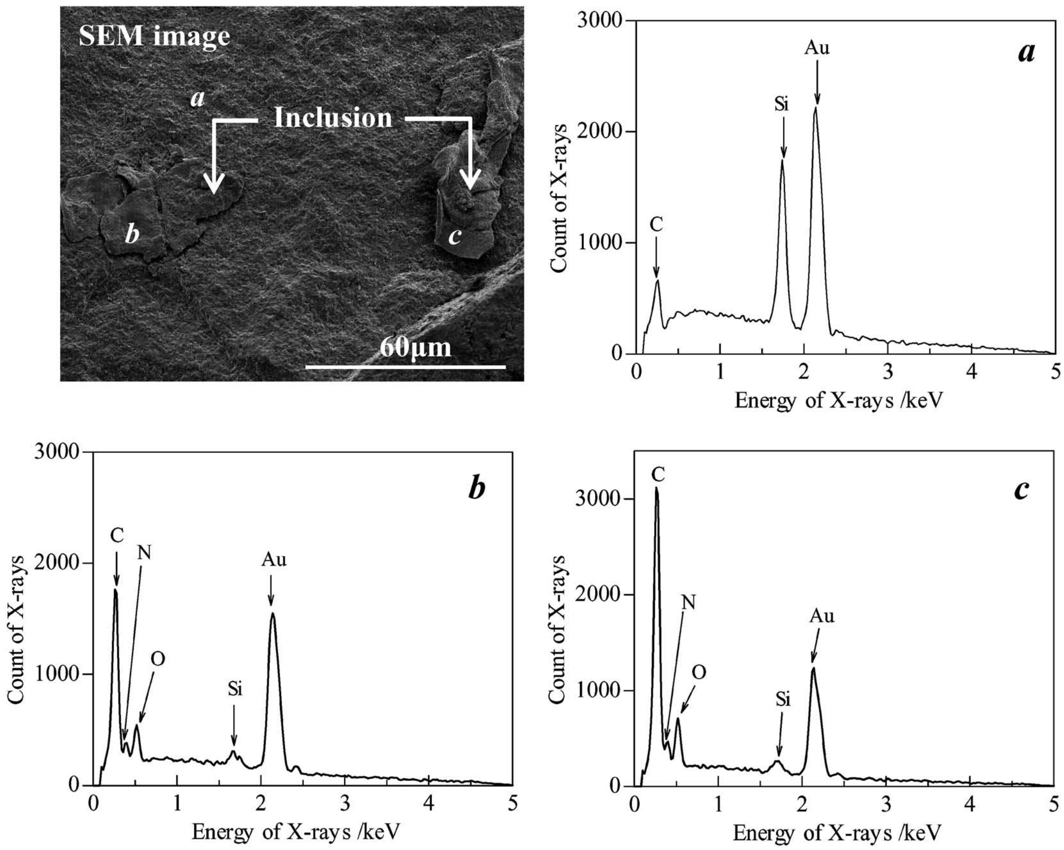

Fig. 4. EDS spectrum obtained from locations *a*, *b* and *c* in FE-SEM image.

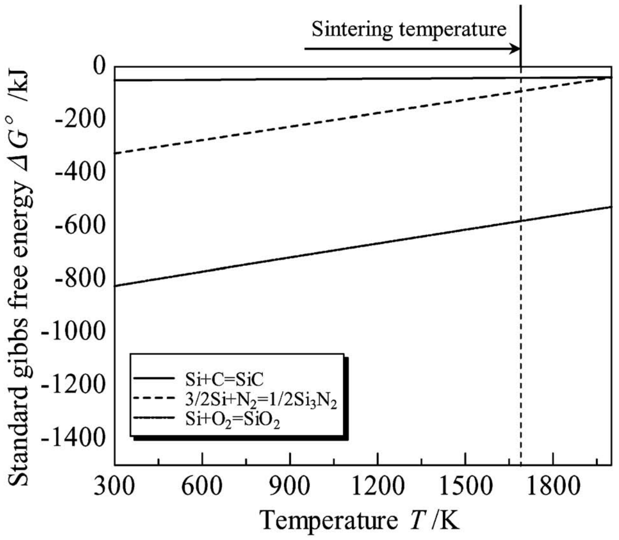

Fig. 6. Ellingham diagram on oxide, nitride and carbide of silicon.

denser than those of N and O. Considering from these results, oxide and nitride of silicon exists around the inclusion.

Ellingham diagram of oxide, nitride and carbide of silicon are given in **Fig. 6.**[7] According to Fig. 6, Si reacts with O and N easier than C at the sintering temperature 1700 K. Therefore it is considered that the reactions between Si and O_2 and/or N_2 occur in the sintering process. In addition, un-reacted C becomes allotrope. Considering from these results, we guess the inclusions is the allotropes of C including oxides and nitrides of silicon and the slip of the allotrope is the one of the cause of the fracture of APF-SiC.

4.3 Approach to improvement of this ceramic material

From above mentioned experimental results and discussions, it is demonstrated that the inclusions consisted of C exist in APF-SiC and it would be concluded that the inclusion is one of the origin of the fracture. Two reasons can be considered as the formation of the inclusion: one is the reactions between Si and O and/or N in the sintering atmosphere and/or dispersant prevent the reaction between melting Si and compressed SiC/C. Another is the inhomogeneous distribution of C in SiC/C generate the inclusion. To reduce the inclusions, following improvement of the process can be considered: (1) To remove N_2 and O_2 from sintering atmosphere. (2) To reduce impurities existed in small pore and grains boundary in SiC/C parent. (3) To make the distributions of the carbon in SiC/C more homogeneously. If we would succeed the above-mentioned improvement, we would obtain the monolithic ceramics that has higher strength and higher damage tolerance ability.

5. Conclusion

In the present experimental study, we find the large inclusions in APF-SiC by using FE-SEM and EDS. Considering from the present experimental results, the inclusions are the allotropes of C covered by oxide and nitride of Si. To prevent generating the inclusions, it is necessary that improvement of atmosphere during the reaction sintering process. And it is also needed the improvement distribution of C in SiC/C.

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