Raman Characterization of Oxidation Behavior of Free Carbon in Silicon Oxycarbide Ceramics

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シリコンオキシカーバイドセラミックス中の遊離炭素の酸化挙動のラマン分光法による解析

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Tantalum and niobium containing silicon oxycarbide ceramics were prepared from hybrid gels through cohydrolysis with methyltriethoxysilane and pentaethoxyniobium/tantalum, and pyrolysis at 1000°C. To investigate the behavior of free carbon in Si–Nb–C–O and Si–Ta–C–O ceramics, Raman spectroscopy was used. The spectra obtained before oxidation showed a higher shift of the G band at around approximately 1610 cm^{−1}, which means a cumulative band of G and D'. After oxidation, however, a symmetric G band, the shift toward a normal position at 1580 cm^{−1} and a weaker background were detected. These phenomena were found to strongly correlate with the oxidation of carbon reactive sites, i.e., those of radical and edge carbon species in tiny graphene layer of free carbon.

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1. Introduction

Silicon oxycarbide (Si–C–O) ceramics are prepared through a sol-gel transition and pyrolysis process. The authors have already reported the preparation of Si–Nb–C–O and Si–Ta–C–O ceramic films from hybrids and their oxidation behavior by X-ray photoelectron spectroscopy (XPS).^{1),2)} The pyrolysis of the hybrids leads to the cleavage of organic groups at approximately 600°C and subsequent carbonization with the evolution of hydrogen and hydrocarbon groups from 600–1000°C.^{3)–5)} The free carbon formed through the pyrolysis is encapsulated in silica and silicon oxycarbide phases, resulting in the resistance to oxidation because of the limitation of oxygen diffusion. Thus, ceramics without a residual organic group show improved antioxidation characteristics, even when a large amount of free carbon is contained in the ceramics.⁶⁾

Soraru reported that the shape of oxycarbide ceramics is important for high-temperature applications, with their bulk and plate shapes being more desirable for thermal stability than those of thin films such as coating film.⁷⁾ However, the heat treatment of hybrids for obtaining shaped bulk ceramics results in the usual cracking problems. We have developed large crack-free self-supported ceramic films by the pyrolysis of niobium- and tantalum-containing hybrid gel.^{1),2)} Additionally, oxidation tests under more severe conditions such as a lower oxidative heating rate should be carried out because shaped ceramics such as plate and self-supported films have resistance to oxidation.

Studies on the oxidation of free carbon in oxycarbide ceramics still remained their weight loss by thermogravimetric

analysis.^{5)–8)} The Raman analysis of free carbon in ceramics before and after oxidation has never been carried out, although Raman analysis is a very important tool for observing carbon materials. Therefore, the Raman analysis of free carbon in oxidized products is fundamentally worth.

In this paper, we report the Raman characterization of the oxidation behavior of free carbon in tantalum- and niobium-containing silicon oxycarbide ceramics.

2. Experimental

Methyltriethoxysilane (MTES) was used as precursor silicon alkoxide (Shin-Etsu Chemical Co., Ltd.). The transition metal alkoxides used as inorganic sources were Ta(OC₂H₅)₅ and Nb(OC₂H₅)₅ (High purity Chemical Laboratory Co., Ltd.). These metal alkoxides and acetylacetone were mixed at a 1 : 2 molar ratio and stirred for 1 h. The mixture of this modified metal alkoxide and MTES was stirred in ethanol (molar ratios; MTES/metal alkoxide = 1/0.05, MTES/ethanol = 1/3 and MTES/H₂O = 1/2). After mixing for 0.5 h, the solution was poured into a Teflon dish and dried at 40°C and 80°C for 48 h and 200°C for 72 h, to obtain self-supported hybrid films. The obtained hybrid films were heated to 1000°C at a heating rate of 3°C/min and kept for 2 h in a flowing Ar atmosphere.

The oxidation test was carried out from room temperature to 1200°C under flowing dry air, using a thermogravimetric analyzer; Rigaku Thermo Plus. Oxidative heating rates of 1, 10 and 20°C/min were applied.

¹³C-magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained by using JEOL JNM-EXCALIBUR-270 MHz with a frequency of 67.80 MHz. Adamantane was used as an external standard. The sample spinning speed was approximately 6 kHz. The spectra of ¹³C-MAS NMR were recorded using a repetition time of 7.0 s.

Raman spectra were measured using an Atago Raman system with an attached charge-coupled device (CCD). The laser

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Fig. 1. ^{13}C -MAS NMR spectra of tantalum- and niobium-containing silicon oxycarbide.

power was kept at 100 mW. To obtain a good signal/noise ratio, 100 scans were carried out. A metallic silicon line was used for Raman shift calibration.

3. Results and discussion

Figure 1 shows the ^{13}C -MAS NMR spectra of the obtained ceramics. Some resonance peaks were detected at approximately 15–30 ppm, which were due to the tetrahedral site CSi_4 . This corresponds to the ^{29}Si -NMR results of our previous report¹⁾ and indicates that the rearrangement between Si–O and Si–C bonds occurred during pyrolysis, because the precursor hybrid was only composed of three siloxane bonds and methyl groups ($\text{CH}_3\text{SiO}_{1.5}$). In polymethylsilsesquioxane-derived oxycarbide ceramics, no Si–O–C and Si–Si bonds were confirmed.⁹⁾ The silicon atoms preferentially bond to oxygen and the remaining silicon atoms bond to carbon. Thus, the remaining carbon, namely excess carbon that has not bonded to other atoms, is defined as free carbon. The detailed pyrolysis behavior of hybrids has already been reported elsewhere.¹⁾ The ^{13}C -NMR spectra qualitatively show the presence of free carbon. As seen from the spectra, a very broad resonance peak detected at approximately 133 ppm is assigned to sp^2 carbon, the so-called free carbon, which is considered to be in tiny graphitic and amorphous state.

The Raman spectra of Si–Nb–C–O and Si–Ta–C–O ceramics before and after oxidation tests are shown in **Figs. 2** and **3**, respectively. The weight loss by oxidation showed only a slight difference among all the ceramics. We have already reported the oxidation behavior of Si–C bonds determined by XPS,²⁾ although the oxidation behavior of free carbon was still unclear.

In the spectra, D and G peaks were detected at approximately 1360 and 1610 cm^{-1} . These bands have already been reported for polycarbosilane-derived SiC fiber and silicon oxycarbide ceramics.^{4), 6), 10)–12)}

D and G bands are normally observed at 1360 and 1580 cm^{-1} , respectively. The D band is due to disordered carbons such as glassy carbon. More disordered carbons such as coke and charcoal show a broader band. In contrast, the G band is assigned to $\text{C}=\text{C}$ stretching vibration (E_{2g}), which is observed in this region for highly oriented pyrolytic graphite and natural single crystals of graphite.

The peak position of the G band was monitored at higher

Fig. 2. Raman spectra of Si–Nb–C–O ceramics before and after oxidation to 1200°C. For the oxidized products of Si–Nb–C–O ceramics, SiNb20, SiNb10 and SiNb1 are notated by heating rates of 20, 10 and 1°C/min.

Nonoxidized sample is described as SiNb.

Fig. 3. Raman spectra of Si–Ta–C–O ceramics before and after oxidation to 1200°C. For the oxidized products of Si–Ta–C–O ceramics, SiTa20, SiTa10 and SiTa1 are notated by heating rates of 20, 10 and 1°C/min.

Nonoxidized sample is described as SiTa.

than 1580 cm^{-1} on the spectra before oxidation, which suggests mixed peaks of the G and D' bands.¹³⁾ The peak at approximately 1610 cm^{-1} is defined as D' band, suggesting tiny graphene layers with many edge carbon atoms, accompanying oxygen and/or radical species because the edge parts may cause partially localized π -electrons to shift to a higher frequency.¹³⁾ During the pyrolysis of hybrids, the organic methyl group is decomposed, resulting in the evolution of hydrogen and hydrocarbon gases.^{1), 3)} In this decomposed stage, edge carbon atoms with accompanying oxygen and/or radical species may be formed.

More symmetrical bands and shifts to 1580 cm^{-1} in the spectrum of SiNb1 were confirmed, shown in Fig. 2. The sites such as the edge carbon with accompanying oxygen and radi-

cal species may be reactive to oxidation.

On the other hand, the spectra of SiTa products before and after the oxidation test were different from those of SiNb products. The G band still remained unsymmetrical and at a position higher than 1580 cm^{-1} for SiTa1 and SiTa10, compared to that of Fig. 2. This suggests higher resistance to oxidation than a SiNb specimen. SEM images did not show any morphological differences (porosity etc.) among the obtained ceramics before and after the oxidation test. The difference of oxidation behavior between SiNb and SiTa suggests that tantalum oxide affects the oxidation of carbon, which prevents the evolution of surface oxygen components. This effect is consistent with tantalum oxide containing glassy carbon.¹⁴⁾

Additionally, G and D bands were superimposed on the large luminescence background in both spectra. After oxidation, the luminescence background became weaker. Babonneau and coworkers suggested that the luminescence background comes from carbon radical species.¹⁰⁾ This may be attributed to the oxidation of reactive sites such as radical carbon species.

An additional weak peak at approximately 1280 cm^{-1} was also observed after oxidation. Amorphous SiO_2 , when accompanied with nonbridging or partially ionized oxygen atoms, showed a Raman shift at approximately 1200 cm^{-1} .¹³⁾ This unstable inorganic bond disappeared under a low oxidative rate of $1^\circ\text{C}/\text{min}$.

4. Conclusion

Shaped oxycarbide ceramics were synthesized from a methyltriethoxysilane- and pentaethoxyniobium/tantalum-based hybrid. The oxidation behavior of free carbon in a transition metal containing oxycarbide ceramics was investigated. Free carbon was detected by ^{13}C -NMR and Raman spectroscopy.

The Raman spectra of the specimens before oxidation showed G, D and D' bands, and luminescence background. However, the D' band and background in the spectra of Si-Nb-C-O ceramics disappeared after oxidation. This phenomenon could be related to the oxidation of the edge

carbon with accompanying oxygen and/or radical species. In contrast, the spectra of Si-Ta-C-O ceramics showed that the G band still remained to be asymmetric and mixed with D' band at a position higher than 1580 cm^{-1} even after oxidation at a lower heating rate, which means the existence of edge carbon atoms. This strongly suggests a higher resistance to oxidation than a Si-Nb-C-O specimen.

References

- 1) Fukushima, M., Yasuda, E., Nakamura, Y. and Tanabe, Y., *J. Ceram. Soc. Japan*, Vol. 111, pp. 857–859 (2003).
- 2) Fukushima, M., Yasuda, E., Nakamura, Y., Teranishi, Y., Nakamura, K. and Tanabe, Y., *J. Ceram. Soc. Japan*, Suppl., Vol. 112, pp. S1531–S1534 (2004).
- 3) Fukushima, M., Yasuda, E., Manocha, L. M., Manocha, S. M., Nakamura, Y., Akatsu, T. and Tanabe, Y., *J. Ceram. Soc. Japan*, Vol. 110, pp. 1044–1047 (2002).
- 4) Pantano, C. G., *J. Sol-Gel Sci. Tech.*, Vol. 14, pp. 7–25 (1999).
- 5) Radovanovic, E., Gozzi, M. F., Goncalves, M. C. and Yoshida, I. V. P., *J. Non-Cryst. Solids*, Vol. 248, pp. 37–48 (2000).
- 6) Manocha, L. M., Yasuda, E., Tanabe, Y., Manocha, S. and Vashistha, D., *Bull. Mater. Sci.*, Vol. 23, pp. 1–4 (2000).
- 7) Soraru, G. D. and Sutto, D., *J. Sol-Gel Sci. Tech.*, Vol. 14, pp. 69–74 (1999).
- 8) Brewer, C. M., Bujalski, D. R., Parent, V. E., Su, K. and Zank, G. A., *J. Sol-Gel Sci. Tech.*, Vol. 14, pp. 49–68 (1999).
- 9) Takamura, N., Taguchi, K., Gunji, T. and Abe, Y., *J. Sol-Gel Sci. Tech.*, Vol. 16, pp. 227–234 (1999).
- 10) Soraru, G. D., Andrea, G. D., Campostrini, R., Babonneau, F. and Maritto, G., *J. Am. Ceram. Soc.*, Vol. 78, pp. 379–387 (1995).
- 11) Ma, J., Shi, L., Shi, Y., Luo, S. and Xu, J., *J. Appl. Polym. Sci.*, Vol. 85, pp. 1077–1086 (2002).
- 12) Sasaki, Y., Nishina, Y., Sato, M. and Okamura, K., *J. Mater. Sci.*, Vol. 22, pp. 443–448 (1987).
- 13) Nakamizo, M. and Tamai, K., *Carbon*, Vol. 22, pp. 197–198 (1984).
- 14) Tanabe, Y., Utsunomiya, M., Ishibashi, M., Kyotani, T., Kaburagi, Y. and Yasuda, E., *Carbon*, Vol. 40, pp. 1949–1955 (2002).