Effect of a Small Concentration of Iron Impurity on the Oxidation Behavior of Porous SiC

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多孔質 SiC の酸化に及ぼす鉄不純物の影響

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Oxidation behavior of porous SiC containing Fe was investigated using a quadrupole mass spectrometer by measuring the volume of evolved gases during oxidation at 1700 K. This Fe-containing SiC was obtained by immersing the SiC in an acetone solution with an $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$ concentration of 0.1 M for 1-5 min followed by calcination at 1173 K. The weight gain and the total amount of gases evolved decreased with increasing Fe_2O_3 content. XRD intensity ratio of cristobalite to SiC was increased with increasing Fe_2O_3 content. These results indicate that the accelerated crystallization of amorphous silica to cristobalite and the retardation of the oxidation were caused by the added Fe.

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1. Introduction

It is well known that sintering aids and impurities contained in SiC and Si_3N_4 ceramics significantly affected their oxidation-resistive properties.¹⁾⁻⁵⁾ A number of reports have been published on the effects of Al, Na and K impurities in these typical non-oxide ceramics,⁶⁾⁻⁸⁾ but the effect of Fe has scarcely been investigated although it is an omnipresent impurity in them.⁹⁾ Ishikawa et al. studied oxidation behaviors of powdery Si_3N_4 materials with different Fe content and tried to clarify the effect of the iron impurity on the oxidation resistances of the materials.¹⁾ Their attempt was not successful probably due to larger contributions of coexisting Al_2O_3 and Y_2O_3 added as sintering aids to the oxidation resistances. Suzuki⁹⁾ carried out oxidation experiments for powdery SiC materials added with as much as 5 mass% Fe_2O_3 (hereafter mass% is abbreviated merely as %). It is likely that, at this Fe_2O_3 content, most of Fe_2O_3 forms a secondary phase and obscures the effect of Fe bonded with the passive SiO_2 layer covering SiC particles. Thus, his results are not of value for reference concerning the effect of the Fe impurity. In addition, it seems worth mentioning that commercially available SiC materials usually contain less than 0.1% Fe.¹⁰⁾

In the present study, high-purity SiC ceramics was selected as a testing material to exclude or reduce the influence of impurities other than intentionally added Fe. This SiC ceramics was porous probably because it was sintered without any sintering aid. The oxidation behaviors of the porous SiC ceramics added with different concentrations of Fe were investigated using a quadrupole mass spectrometer by quantitatively measuring evolved gases during oxidation. This paper, mainly dealing with interrelations of the Fe content, the oxidation behavior and the microstructure of the surface SiO_2 layer, intends to clarify the effect of Fe on the oxidation-resistive property of SiC ceramics from the microscopic viewpoint.

It should be noted that promotion of the durability of non-oxide ceramics at high temperatures is of great industrial importance. Another intention of this study is to establish

the method to enhance the oxidation resistance of SiC ceramics.

2. Experimental procedure

High-purity porous SiC ceramic plate purchased from Ibiden Co., Ltd.¹¹⁾ was cut into rectangular bars of $3 \times 4 \times 40$ mm. These bars were heated at 1200 K in air for 1h to remove the free carbon. Iron acetylacetonate ($\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$, FeAcac) from Nacalai Tesque Inc. was used as the source of Fe. The SiC bar was immersed in an acetone solution with the FeAcac concentration of 0.1 M for 60-300 s followed by being dried and successively calcined at 1173 K for 1h. This Fe-doping process converts FeAcac into iron oxide.

Electron probe microanalyzer (EPMA) measurements of the cross section of the resulting samples could not detect the local enrichment of Fe, indicating that Fe was homogeneously distributed in pores of the sample. X-ray diffraction (XRD) analysis of the samples revealed that the impregnated Fe was changed to Fe_2O_3 . The Fe_2O_3 content in the Fe-doped sample was calculated from the following Eq. (1),

$$\text{Fe}_2\text{O}_3 \text{ content (\%)} = 100(W_1 - W_0)/W_0 \quad (1)$$

where W_0 and W_1 are the weight of the SiC bar before the immersing treatment and that after the Fe-doping process, respectively. The Fe-doped sample was heated to 1700 K with a temperature-rising rate of 5 K/min and then soaked for 15h. The oxidation test of the Fe-doped sample was almost the same as mentioned in the previous paper,¹¹⁾ in the present experiments, oxygen partial pressure (P_{O_2}) being fixed at 2 kPa. It seems necessary to note that the oxidation kinetics for high-purity porous SiC at P_{O_2} of 2 kPa obeyed the parabolic law and its oxidation type was classified into the mild oxidation.¹¹⁾ In the present study, oxidation behaviors of the Fe-doped samples were analyzed also from the kinetic standpoint.

Weights of the Fe-doped sample before and after the oxidation test were measured, the difference between them being a measure of the oxidized fraction of the sample.

XRD analysis and scanning electron microscope (SEM) analysis for the sample after the oxidation test were performed to investigate the effect of Fe.

3. Results and discussion

3.1 Amount of gas evolved and weight change

During oxidation, CO_2 and CO were evolved according to Eqs. (2) and (3). Evolution rates of CO_2 and CO are shown in Fig. 1 and Fig. 2, respectively. The point of time 0 in Fig. 1 means that at that time, the temperature around the sample reached the soaking temperature (1700 K). In the cases of $\text{Fe}_2\text{O}_3=0$ and 0.13%, the evolution rate reached a maximum immediately after the onset of the soaking at 1700 K and decreased with the soaking time. In the cases of $\text{Fe}_2\text{O}_3=0.24$ and 0.37%, the evolution rate reached a maximum before the onset of the soaking at 1700 K and decreased abruptly. These facts indicate that the passive oxidation as represented by the following equations, occurred at this oxygen partial pressure.

Integration curves plotting total amount of CO_2 and CO gases evolved (hereafter abbreviated as gas amount) as a function of the oxidation time were shown in Fig. 3. This figure shows that the gas amount decreased with increasing Fe_2O_3 . In the case of 0.13% Fe_2O_3 sample, the gas amount

was almost the same as that in the case of Fe-undoped sample, while, in the case of 0.24% Fe_2O_3 sample, the gas amount decreased to 1/6 of that in the case of Fe-undoped sample. These facts indicate that a critical Fe_2O_3 content lies between 0.13 and 0.24% at which Fe exerts a remarkable effect in enhancing the oxidation resistance.

In the case of 0.13% Fe_2O_3 sample, the gas evolution continued for the oxidation time of 10h. In the cases of 0.24% and 0.37% Fe_2O_3 samples, the gas evolutions almost stopped at the oxidation times of 6h and 1h, respectively. The period where the gas evolution could be observed decreased with increasing the Fe_2O_3 content.

In order to examine whether the oxidation behaviors of the Fe-doped samples can be classified into the parabolic type or not, the parabolic plots for the total amount of CO_2 and CO evolved were made and shown in Fig. 4. The plotted line must draw the straight line when the oxidation kinetics obeys the parabolic law. In the case of the Fe-undoped sample, the integration curve obeyed the parabolic law in the oxidation time range from 2 to 12h.

In the cases of the Fe-doped samples, the plots drew the straight lines only around the time 0, that is near the onset of the oxidation, changing later to the flat line. These results indicated that the oxidation behaviors of the Fe-doped samples could not be classified into the parabolic type. Porz and Thummler¹²⁾ found the deviation of the plotted curve from the parabolic law when porous silicon nitride ceramics was oxidized. They explained this phenomenon as follows. When the pore is filled with oxidation products the oxidation in the pore stops abruptly and the overall reaction

Fig. 1. CO_2 evolution rate during oxidation of porous SiC containing various amounts of Fe_2O_3 at 1700 K.

Fig. 2. CO evolution rate during oxidation of porous SiC containing various amounts of Fe_2O_3 at 1700 K.

Fig. 3. Amount of gases ($\text{CO}_2 + \text{CO}$) evolved during oxidation of porous SiC containing various amounts of Fe_2O_3 at 1700 K.

Fig. 4. Parabolic plots of gas evolved during oxidation of porous SiC containing various amounts of Fe_2O_3 at 1700 K.

proceeds according to the asymptotic law rather than the parabolic law. Similarly to the above case, oxidation behaviors deviating from the parabolic kinetics have often been found. Narushima et al.¹³⁾ analyzed the oxidation behavior of SiC by the use of the parabolic plot and observed the gradient change in the plotted line. They attributed it to the crystallization of amorphous silica to cristobalite which caused the enhanced oxidation resistance. Examination of the oxidation kinetics for the Fe-doped samples showed that 0.13% Fe₂O₃ case roughly fitted with the asymptotic law but its adaptability to 0.24 and 0.37% cases could not be judged because of the too rapid completion of the oxidation. Similarity observed in Fig. 3 among the curves for 0.13, 0.24 and 0.37% Fe₂O₃ samples, however, suggests that the asymptotic law is more suitable as the oxidation kinetics for the Fe-doped samples.

Cristobalite was detected as an oxidation product by XRD measurement of the surface layer of the sample after the oxidation. Figure 5 shows the X-ray intensity ratio of (101) peak of cristobalite to (111) peak of SiC along with the weight change of the sample before and after the oxidation and the total amount of gases evolved during the oxidation. The X-ray intensity ratio of cristobalite to SiC was increased with increasing the Fe₂O₃ content from 0.13 to 0.24% and then was decreased. SiC and cristobalite were detected on the surface of the samples after the oxidation in the cases of Fe₂O₃=0.13 and 0.24%. SiC, cristobalite and Fe₂O₃ were detected in the cases of Fe₂O₃=0.37 and 0.43%. The weight gain was decreased with increasing the Fe₂O₃ content until Fe₂O₃=0.37% and then increased at around Fe₂O₃=0.43%. The total amount of gases evolved showed the similar tendency as the weight gain. At Fe₂O₃=0.24 and 0.37%, the weight gain showed the lowest value, indicating that the appropriate content of Fe₂O₃ to promote the oxidation resistance of the SiC sample lies between 0.24 and 0.37%. These results suggest that the degree of crystallinity of cristobalite acting as the protective film was increased although the thickness of the cristobalite film was decreased with increasing the Fe₂O₃ content. In order to ascertain the above assumption, the half width was measured for (101) peak of cristobalite in the Fe-doped samples after the oxidation.

Figure 6 shows the relation between the half width of (101) peak of cristobalite and the Fe₂O₃ content. The half width was decreased with increasing the Fe₂O₃ content

from 0.13 to 0.24% and then was increased. These results demonstrate that there is the most appropriate Fe₂O₃ content around 0.24% for the crystallization of cristobalite.

3.2 Porosity and microstructure

Figure 7 shows the relation between apparent porosity and the Fe₂O₃ content of the Fe-doped sample. The apparent porosity was measured by Archimedeian method using water, the measured samples being oxidized ones which were not pulverized. At 0.13% Fe₂O₃, the apparent porosity showed the lowest value and then was increased with the increasing Fe₂O₃ until 0.37%. By considering that the oxidation product accumulate in the pore, conformity of the tendency for the apparent porosity with that for the weight gain except the undoped case can be well explained. Preservation of comparatively higher porosity irrespective of the large weight gain observed for the undoped sample after oxidation suggests that the pore-filling mechanism was different between the Fe-doped and Fe-undoped samples. The previous paper¹¹⁾ dealing with high-purity porous SiC showed that SiO₂ deposited on the external surface and in pores equally. The present results show that the SiO₂ deposition in pores was enhanced by the Fe-doping.

If, as suggested by Porz and Thummler,¹²⁾ the asymptotic oxidation behavior of porous SiC was caused by closure of openings of pores, the apparent porosity would become a minimum at the Fe₂O₃ content around 0.24%, but this is not the case. It seems reasonable to alternatively consider that the asymptote-like oxidation kinetics of the Fe-doped sample was governed by the degree of crystallization of the protective SiO₂ layer formed during the oxidation.

Figure 8 shows the SEM photographs of the surface of the samples after the oxidation. The sample with 0.13% Fe₂O₃ had almost the same surface microstructure as the Fe-undoped sample. In the case of 0.24% Fe₂O₃ sample, its surface was covered by the oxidation product in which comparatively small pores were seen and most of pores which were present before the oxidation, disappeared. Flatly deposited oxidation product suggests that it was crystallized from low viscosity melt. Cracks which arose probably accompanying the transformation of cristobalite from β to α were observed in the oxidation product on the surface. In the case of 0.37% Fe₂O₃ sample, the dendritic product was formed mounting on the glassy product.

The amount of Fe needed to cover the total surface area of the pores was calculated as follows. FeAcac absorbed

Fig. 5

Fig. 6

Fig. 7

Fig. 5. XRD intensity ratio of cristobalite (101)/SiC(111), amount of gas evolved and weight change after oxidation.

Fig. 6. Half width of cristobalite (101) as a function of Fe₂O₃ content.

Fig. 7. Relation between apparent porosity and Fe₂O₃ content of porous SiC after oxidation at 1700 K.

Fig. 8. Scanning electron micrographs of the surface of the porous SiC containing Fe_2O_3 after oxidation at 1700 K for 15h in Ar-O_2 ($P_{\text{O}_2}=2$ kPa).

into the pores decomposes to FeO in the intermediate stage of the calcination process. FeO would be well dispersed on the internal surface of the pores due to the significant acid-base interaction between SiO_2 (acid) and FeO (base). The average pore diameter of the starting porous SiC materials is $1.5 \mu\text{m}$.¹¹⁾ The total surface area of the pores in the starting sample ($3 \times 4 \times 40$ mm) was calculated to be 0.61 m^2 from the porosity (48.4%) and the bulk density (1.56 g/cm^3) data, and by assuming the pores cylindrically shaped with their diameters all $1.5 \mu\text{m}$. When the monolayer composed of unit cells of wuestite ($a=0.43 \text{ nm}$,¹⁷⁾ 4FeO contained) covers the area of 0.61 m^2 , its amount is calculated to be 1.6 mg , which corresponds to $1.7 \text{ mg Fe}_2\text{O}_3$ or 0.23% Fe_2O_3 in the Fe-doped sample. This value of 0.23% is very close to the Fe_2O_3 content of the sample which showed the highest crystallinity of cristobalite after the oxidation. FeO intermediately formed in the pores must convert to Fe_2O_3 in the final stage of the calcination process but would be regenerated in the early stage of the oxidation where both CO and CO_2 can be detected in the ambient atmosphere.

3.3 Reaction between FeO and SiO_2 layer

As a due course, reaction of SiO_2 as the oxidation product with FeO must be discussed along with its effect on the oxidation behaviors of Fe-doped samples. The present authors recently clarified that cooperative action of Fe^{2+} and Fe^{3+} markedly promoted the crystallization of amorphous SiO_2 to cristobalite.¹⁴⁾

The conversion to cristobalite would be suppressed if the doped amount of Fe_2O_3 was not sufficient to cover the entire surface of the pores. This situation corresponds to the sam-

ple with 0.13% Fe_2O_3 content, passivation of which needed as long as 10h.

Formation of a liquid phase was suggested during the oxidation by the SEM observation of the oxidized samples. In the case of 0.37% Fe_2O_3 sample, the amount of SiO_2 formed until its passivation was calculated to be about 13 mg , which is much larger than the Fe_2O_3 content. The phase diagram for $\text{SiO}_2\text{-FeO}$ ¹⁵⁾ shows that in the SiO_2 -rich region, a liquid phase and tridymite coexist at 1700 K at the equilibrium state, but since it costs long time to attain the equilibrium, cristobalite has often been found to be the major species in this region.¹⁶⁾

Since in the present study, the pore volumes of the samples were reduced after the oxidation, contribution of the pore-mouth blocking to their oxidation behaviors can not be excluded, but the incomplete blocking observed for the passivated sample strongly indicate that the other mechanism must be operative. A crystallization-induced passivation model proposed by the present authors seems to be more valid than the pore-mouth blocking model. More detailed mechanistic investigation is now in progress and will be published elsewhere.

4. Conclusion

Oxidation behaviors of porous SiC ceramics intentionally doped with $0.13\text{--}0.43\%$ Fe_2O_3 in Ar-O_2 atmosphere ($P_{\text{O}_2}=2$ kPa) at 1700 K for 15h were investigated and following results were obtained.

(1) Doped Fe_2O_3 enhanced the oxidation resistance of the SiC ceramics. At the Fe_2O_3 contents of 0.24 and 0.37% , Fe-doped samples exhibited about $1/6$ of the weight gain of Fe-undoped sample.

(2) Doped Fe_2O_3 promoted the yield and the crystallinity of cristobalite formed during the oxidation. Cristobalite was considered to act as a protective film against the oxidation and a crystallization-induced passivation model was proposed.

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