

HIGH SURFACE AREA SiC CERAMICS MADE FROM CARBONIZED RICE HULLS BY TREATMENT OF HF - HNO₃ MIXTURE

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Introduction

Silicon carbide(SiC) as catalysts support has been recognized to have several advantageous properties compared to the conventional catalyst supports such as Al₂O₃ and SiO₂. These advantages come from the higher stability of the support at high temperatures, high hardness, high thermal conductivity and inertness of the surface(1,2). Particularly, SiC has high thermal conductivity of 500 W/mK for single crystal state at room temperature, which is close to that of metals such as Ag or Cu (400–500 W/mK)(4). Therefore, by the favor of heat-sink of the heat produced by very exothermic reactions, the catalysts on SiC support can be prevented from sintering (3).

Because of the intimate contact of the so reactive carbon and SiO₂ when the rice hulls are carbonized, the formation and sintering of β -SiC could proceed at the same time with a hot press(4). In this case, the formation catalysts such as Fe and Co compound were very effective. And a solution-precipitation process through M-Si-C liquid phase is essential for the nucleation and grain growth or whisker when there is enough space to grow (4,5). In the intermediate solution-precipitation process, an isolated or a skeletal microstructure is expected when coalescence is slow (6).

One of the possible strategies to increase the surface area is to remove iron or cobalt silicides in the β -SiC grain which are converted from its oxide state used as catalysts for the formation of β -SiC(4,5). These resulting small pores are made larger by soaking in the HF-HNO₃ mixture.

Experimental

The fabrication procedure of β -SiC ceramics was done in the same way as the previous method(4). The carbon to the SiO₂ weight ratio(C/SiO₂) of the carbonized rice hulls used for the production of β -SiC ceramics at various temperatures was 0.42. The concentration of Fe₂O₃ and CoO catalyst was 2.2 mM and 10 mM in 18 g of the carbonized rice hulls, respectively, if otherwise stated.

After fabricating the SiC ceramics (ca. 4x30x30mm), a

small piece of β -SiC (ca.3x4x15 mm) was soaked in a mixture of 50H₂O:25HNO₃:25HF(in volume) for various period((days) at 50 – 65 °C. The surface area and the pore size distribution of the samples were measured by N₂ adsorption with NOVA 1000(QUANTACHROME CORPORATION). The surface area was calculated from the nitrogen adsorption isotherm using the BET method. The pore size distribution was obtained from desorption branch of the isotherms.

Results and Discussion

1. Effect of hot-press temperatures

It was expected that some metallic silicides are impregnated in the β -SiC grain during the course of grain growth of β -SiC by the solution-precipitation. In other words, the feature of these metallic silicides is virtually dependent upon the sintering temperatures. This means that, if these metallic silicides impregnated in the β -SiC grain are removed, micro-pores will be produced and eventually the surface area will increase. The surface area was measured for β -SiC ceramics which were fabricated at temperature ranges of 1900 °C to 2050 °C and 1850 °C to 2050 °C for Fe and Co catalysts, respectively. The results are given in Fig. 1 for Fe catalyst and in Fig. 2 for Co catalyst. The surface area of the thus acid-treated β -SiC at the same amount of dissolution was decreased with the increase of the hot press temperatures from 1900 °C to 2050 °C for Fe catalyst and 1850 to 2050 for Co catalyst. This is because the iron and cobalt silicides might progressively coagulate into a larger size, and finally were expelled from the inside of β -SiC grain with the increase in temperature and the grain growth has occurred. As discussed later, these small surface area of Fe catalyst were found to be composed of mainly the external surface of β -SiC grain. A similar temperature dependencies of the surface area of β -SiC with Co catalyst upon the amount of dissolution was found.

It would be also considered that the stacking faults at lower temperature are larger than those at higher temperature, so that the surface area would become larger with the decreasing hot-press temperature, because the β -SiC ceramics with larger stacking faults might

be attacked by the HF-HNO₃ mixture more easily than those with smaller stacking faults. These things should be clarified in the near future.

2. Effect of C/SiO₂

To maximize the surface area, the effect of the residual carbon in the β-SiC ceramics was investigated. The C/SiO₂ was adjusted by the burn-off of the carbon in the carbonized rice hulls at around 350 °C for various periods, followed by hot-pressing at 2050 °C for 1 hr. The surface area was measured after the removal of carbon present in the hot-pressed samples at 700 °C in air and the soaks for the various periods. The results of the surface area measurement and some data are given in Figs.3 and 4, and Table 1. The surface area was increased with the increase in C/SiO₂ value at any amount of dissolution, that is, the more residual carbon was, the larger surface area was found for both Fe and Co catalysts. These are because that when the carbon contents in the ceramics becomes large, the more HF-HNO₃ mixture can penetrate into the SiC ceramics, and also this residual carbon retards the grain growth during the hot-pressing (8). In case of Co catalyst, Co₂Si, CoSi and CoSi₂ were found in the β-SiC ceramics, depending upon the C/SiO₂ value. Table 1 shows that when the C/SiO₂ value is larger, the higher metallic silicides are produced for both Fe and Co catalysts.

With regard to fracture toughness of around 50 wt% dissolution of β-SiC ceramics which had the highest level in surface area, the fracture toughness seemed to have the highest for the sample hot-pressed at 2050 °C of the carbonized rice hulls with C/SiO₂ = 0.61 for Co catalyst. This is because that the solution – reprecipitation of the metallic silicides made it possible to develop enough neck growth at 2050 °C even in the presence of the residual carbon.

3. Pore distribution and SEM measurements

The pore distribution curve obtained by N₂ adsorption showed the pore size was about 16nm for Fe catalyst and 20 nm for Co catalyst at around 50wt% of dissolution. The pore size distribution curve for Fe catalyst is shown in Fig. 5 at various C/SiO₂ values. The pore size distribution curves changed a little at the various C/SiO₂ values. The difference of this pore size distribution from Fe catalyst and Co catalyst has not been clear yet. But it would probably be due to the difference in the concentration of the catalysts.

A scanning electron microscopy was used to observe the surface with or without the treatment of β-SiC ceramics by HF or HF-HNO₃ mixture. The image of β-SiC surface untreated with the HF at the hot press temperature of 1900 °C showed smooth surface, but treated surface by HF showed very small pores on the surface of β-SiC grain (Fig. 6). The X- ray diffraction profiles showed

there was a diffraction line due to FeSi in the untreated SiC. But the line due to FeSi disappeared in the HF-treated sample. And when the hot-press temperatures were raised up to 2000 °C, this isolated pores changed to skeletal form(Fig. 7). At the temperature of 2050 °C for Fe catalyst, there were sub-micron meter particles , which were found to be iron silicide by the measurement of EDX, on the β-SiC grain grown larger than 10 microns meter. After the treatment of HF-HNO₃ of this 2050 °C sample, it revealed that there was no pore in the β-SiC grain, but its external surface had been etched (Fig. 8). Therefore, it can be concluded that the surface area was mostly composed of the external region of the SiC grain at 2050 °C for Fe catalyst. But in case when the residual carbon existed, the surface of β-SiC grain revealed that the skeletal pores were produced after the HF-HNO₃ treatment.

Similar behaviors with the increase in temperature were found on the SEM measurements of β-SiC fabricated with the use of Co catalyst. But, as far as the SEM image of the external view of β-SiC grain at 50wt% dissolution, the β-SiC ceramics at 2100 °C for the Co catalyst corresponded to the ceramics at 2050 °C for the Fe catalyst.

Conclusions

In this study, the mesoporous β-SiC ceramics , which has surface area of nearly 50 m²/g were synthesized by the HF-HNO₃ treatment of β-SiC ceramics made by hot-pressing carbonized rice hulls, having an intimately contacted mixture of carbon and SiO₂. There have been some papers which dealt with the synthesis of high surface area SiC, but to the present authors' knowledge, these are about the surface area of fine SiC powders or granules. Because the present high surface area β-SiC ceramics will be able to be fabricated in a variety of size and form, it would be more useful than the powders and granules. Also this porous β-SiC ceramics is fabricated through the solution–reprecipitaion process of M-Si-C liquid for the nucleation, grain and neck growth, so that it has higher performance of oxidation resistant property than the β-SiC powders and granules, which were synthesized from the CVD process (1,2,9). Usually the CVD-process gives the higher stacking faults of β-SiC than through the solution– reprecipitaion process(8,9). Also this method has given the first high surface β-SiC ceramics with macro pore produced from the removal of the residual carbon and a certain meso-pore distribution.

References

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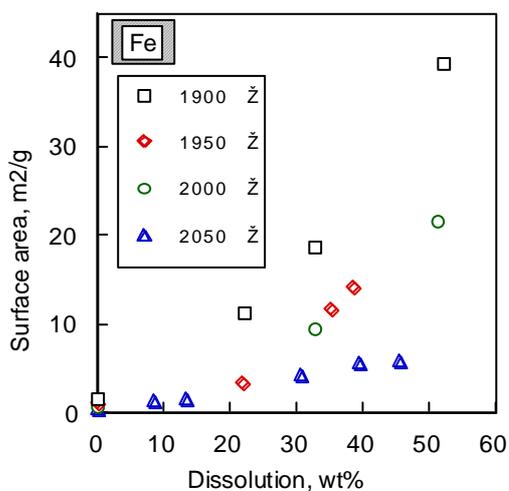


Fig. 1. Relationship between surface area and weight loss by leaching with HF-HNO₃ mixture

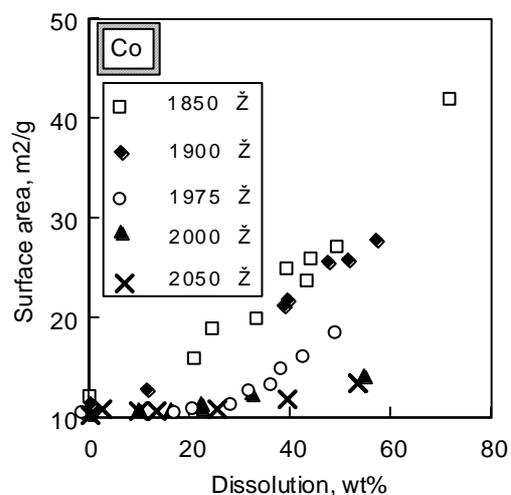


Fig. 2 Relationship between surface area and the amount of dissolution at various temperature.

Table 1 The C/SiO₂ value, residual carbon(R. C) and Chemical formula of metallic silicides at 2050

<u>Fe catalyst</u>			<u>Co catalyst</u>		
C/SiO ₂	R. C(wt%)	Chemical formula	C/SiO ₂	R. C (wt%)	Chemical formula
0.79	26.2	FeSi	0.61	10.3	Co ₂ Si,CoSi
0.65	10.7	FeSi	0.53	1.8	CoSi
0.52	0.0	FeSi	0.52	0.0	CoSi
0.42	0.0	FeSi ₂	0.42	0.0	CoSi ₂

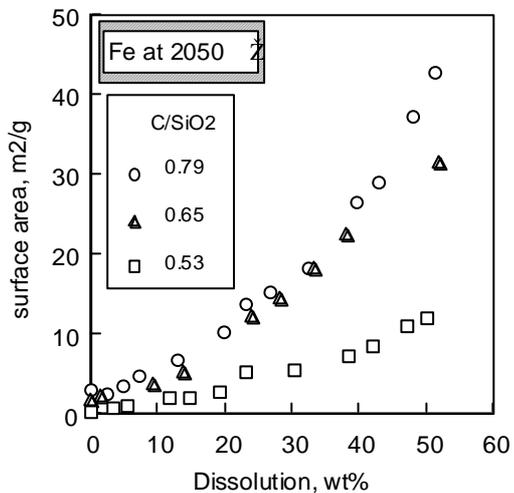


Fig. 3 Relationship between surface area and the amount of dissolution at various C/SiO₂ in the carbonized rice hulls.

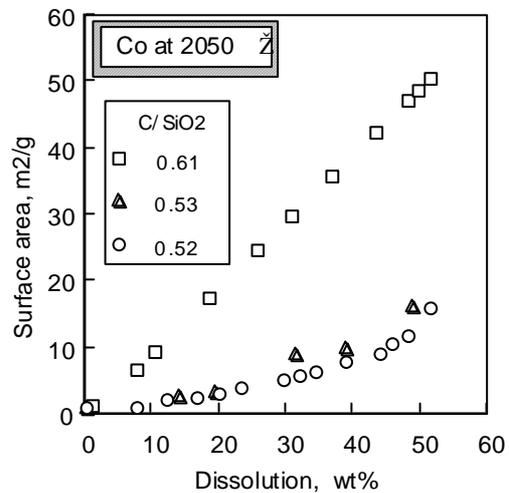


Fig. 4 Relationship between surface area and the amount of dissolution at various C/SiO₂ in the carbonized rice hulls.

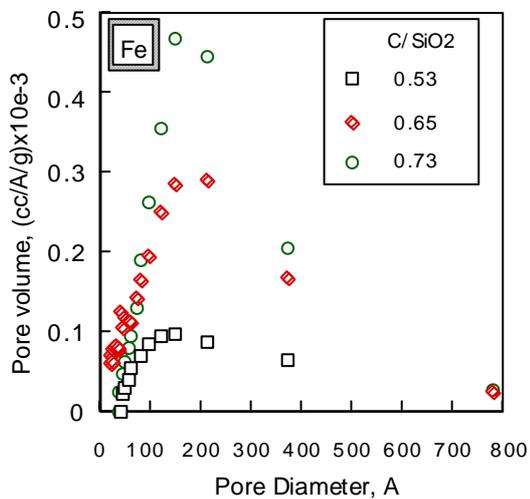


Fig. 5 Pore distribution curve at various C/SiO₂ value in the carbonized rice hulls.

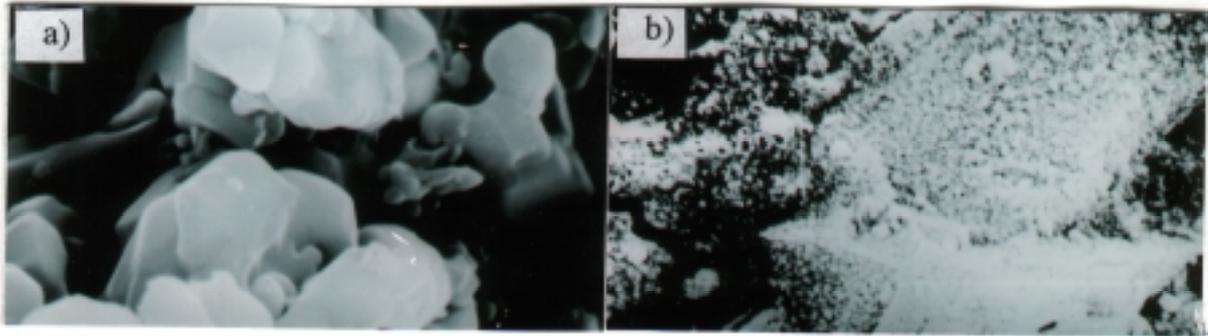


Fig. 6. SEM images (a) before and (b) after the HF treatments of β -SiC hot-pressed at 1900 °C with 5 mM Fe₂O₃.

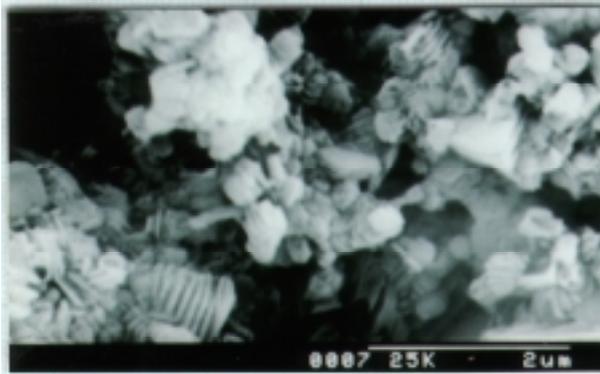


Fig. 7. SEM image after the HF-HNO₃ treatment of β -SiC hot-pressed at 1950 °C.

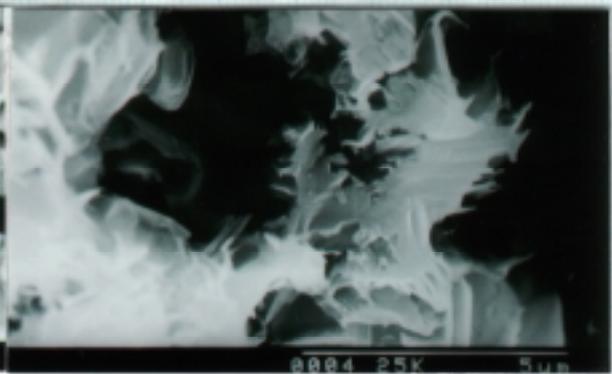


Fig. 8. SEM image after the HF-HNO₃ treatment of β -SiC hot-pressed at 2050 °C.

