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Effect of Additive Composition on High Temperature Oxidation Resistance of Pressureless Sintered Silicon Carbide Ceramics for Particle-Based Accident Tolerance Fuel

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1. Introduction

Silicon carbide (SiC) is a promising material for fission and fusion power applications due to its superior physical and thermal properties such as low specific mass, low neutron cross section, excellent radiation stability, low coefficient of thermal expansion, and high thermal conductivity [1-3]. Also, SiC received considerable attention due to it's a potential for achieving higher safety margins under beyond-design-basis accident (BDBA) scenarios. Especially, the Particle-based accident tolerant (PBAT) fuel using SiC is alternative course to overcome the severe accident. The presence of the SiC layer of the TRISO and the dense SiC matrix of ceramic capsule in Particle-PBAT fuel provide two additional barriers to fission product release. Above all, the performance on high temperature oxidation of PBAT fuel is one of important factors for plant safety of nuclear reactors. Given the significant interest in SiC materials for the PBAT fuel, the high temperature oxidation of SiC, especially in the presence of water vapor, has received considerable attention. Sintering method of SiC ceramic matrix for PBAT fuel is liquid phase sintering (LPS) method by additive system. Thus, investigating of high temperature oxidation of LPS-SiC ceramics with additives would be of interest.

In the present work, the effect of additive composition on high temperature oxidation of pressureless sintered SiC ceramics for PBAT fuel has been investigated.

2. Experimental Procedure

Commercially available β-SiC (0.5 μm, 99.9%, Grade BF-17, H. C. Starck, Berlin, Germany), Al_2O_3 (0.3 μm, 99.99%, AKP-30, Sumitomo Chemical Co., Ltd., Tokyo, Japan), Y_2O_3 (0.4 μm, 99.99%, Kojundo Chemical Lab Co., Ltd., Sakado-shi, Japan), AlN (Grade F, Tokuyama Soda Co., Ltd., Tokyo, Japan), $CaCO_3$ (99% up, High Purity Chemicals, Japan) were used as the starting powders. Five batches of powder mixtures were prepared by ball milling using SiC media in a polypropylene jar for 24 h in ethanol. The mixture of the raw materials was β-SiC and 3 to 5 vol% various additives. The mixture was dried, sieved (60 mesh), and pressureless sintered at 1875°C for 2 h in a argon atmosphere. The relative density of the sintered specimen was determined using the Archimedes method.

The sintered specimens were polished and etched with CF_4 plasma containing 10% oxygen. The morphology of the etched microstructure was examined by scanning electron microscopy (SEM, S4300, Hitachi Ltd., Hitachi, Japan).

High temperature oxidation resistance was measured using thermogravimetry (TGA, Netzsch STA 449 F3) from 200°C to 1200 °C for 50 h with Ar-68%H_2O. The water injection rate was ~2.5 mL/h during the tests.

3. Results

The relative densities of the pressureless sintered specimens were > 97% for all samples. Table 1 shows the sintered densities of LPS-SiC ceramics.

Table 1. The sintered densities of liquid-phase sintered SiC ceramics

Specimen	Composition	Relative Density (%)
SC-AYN-1	97% SiC + 3% (Al_2O_3-Y_2O_3-AlN)	>99
SC-AY-1	97% SiC + 3% (Al_2O_3-Y_2O_3)	>99
SC-AY-2	95% SiC + 5% (Al_2O_3-Y_2O_3)	>99
SC-AYC-1	97% SiC + 3% (Al_2O_3-Y_2O_3-CaO)	>97
SC-AYC-2	94.5% SiC + 5.5% (Al_2O_3-Y_2O_3-CaO)	> 98

This result suggested that even though lower sintering temperature of SiC with alumina-yttria-calcia additives were sufficient to fully densify SiC ceramics by conventional sintering in flowing argon, indicating that the alumina-yttria-calcia system is very effective for the densification of SiC.

The XRD analysis for all specimens showed the presence of β-SiC (3C) as a major phase and α-SiC (6H, 4H) as a minor phase, indicating the partial occurrence of the β→ α phase transformation of SiC during sintering. The relative lower sintering temperature is suppressed the β to α phase transformation of SiC. All specimens show secondary phases such as YAG, $Y_2Si_2O_7$ by additives addition.

The microstructures of the SiC specimens with various additives are shown in Fig. 1. The grain growth of SiC increased with increasing additive content and large equiaxed grains grew in the small matrix grains of the microstructure by Ostwald-ripening mechanism. The XRD patterns and microstructure observation indicate that the β→α phase transformation was not completed in the present samples.

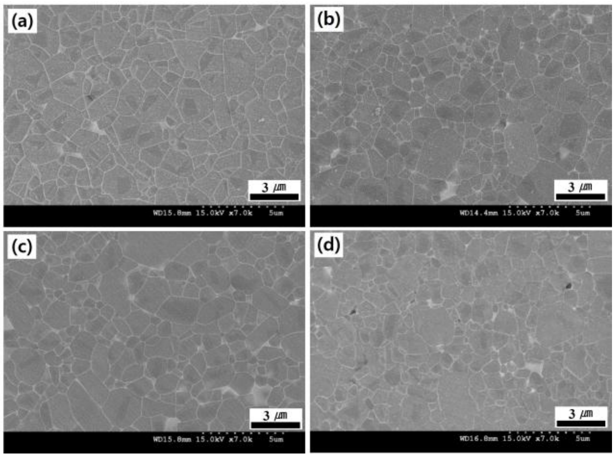

Fig. 1. Typical microstructures of SiC ceramics: : (a) SC-AYN-1, (b) SC-AY-1, (c) SC-AY-2, and (d) SC-AYC-2.

The high temperature oxidation resistance of SiC specimens was incresed with increasing additive content and with decreasing steam flow rate and dependent on the chemistry of the additive composition. The SiC ceramics sintered with AYC additives exhibited the high temperature oxidation resistance of 0.45 mg/cm^2 at 1200ºC for 50h in Ar-68%H_2O among all the samples with the additives containing Al because of the crystalline state of intergranular glassy films (IGF) in SC-AYC [4-5]. SC-AYC had a completely crystallized intergranular films and ternary junctions, whereas SC-AY and SC-AYN had an amorphous IGF and partly crystalline junctions [4-5]. The diffusivity of cation through amorphous intergranular films is considered to be faster than that in crystalline intergranular films because of low viscosity of amorphous intergranular films. Therefore, weight improvement by oxidation is accelerated through amorphous intergranular films.

After high temperature oxidation, surface of all SiC specimens are shown in Fig. 2. Exposure to the oxidation condition of SiC specimens resulted in the formation of a porous SiO_2 scale on the specimen surfaces (Eq 1.).

$$SiO_2 + 2H_2O \rightarrow Si(OH)_4 \text{ (volatilization)} \quad (1)$$

Preliminary data on the oxidation of the SiC ceramics will be presented.

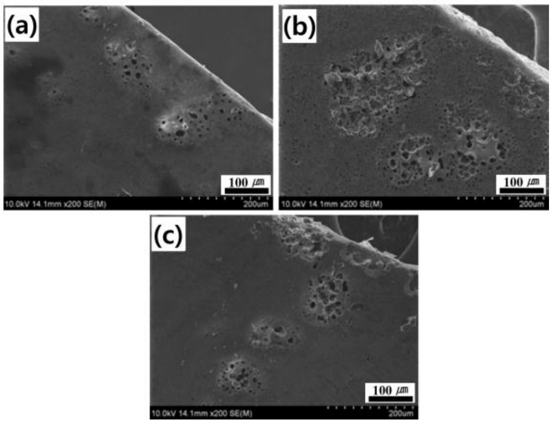

Fig. 2. Typical microstructures after oxidation of SiC ceramics: (a) SC-AYN-1, (b) SC-AY-2, and (c) SC-AYC-2.

4. Conclusions

SiC ceramics with 3 to 5 vol% various additives could be fully densified by conventional sintering at 1875℃ for 4 h in a argon atmosphere. The high temperature oxidation resistance perfomance of SiC ceramics sintered with alumina-yttria-calcia additives showed a minimum weight gain. The high temperature oxidation resistance of LPS-SiC specimens was dependent on the additive content, steam flow rate, and chemistry of the additive composition. More importantly, crystallization of grain boundary is essential factor for oxidation resistance performance of LPS-SiC ceramics. Developed LPS-SiC ceramics with alumina-yttria-calcia additives are very useful for densification and oxidation resistance on matrix material of the PBAT fuel.

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