

Oxidation Behavior in High Temperature Steam Environment of Liquid Phase Sintered Silicon Carbide Ceramics for TRISO-Based Accident Tolerant Fuel

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1. Introduction

For materials about fission and fusion power applications, silicon carbide (SiC) ceramics is a promising material owing to its superior mechanical properties, excellent radiation stability, low neutron absorption cross section, low specific mass, and excellent thermal properties [1-3]. Recently, various of literatures have been published to improve accident tolerance through nuclear fuel using SiC ceramics, such as SiC/SiC_f cladding and TRISO-SiC fuel pellet., based on those excellent properties [1-5].

Especially, TRISO-SiC fuel pellet is a promising fuel concept for achieving higher safety margin under beyond-design-basis accident (BDBA) scenarios. The presence of the SiC layer in the TRISO and the dense SiC matrix of ceramic capsule in TRISO-SiC fuel pellet provide double barriers to fission product release. However, SiC has a poor sinterability because of extremely low self-diffusion coefficient and high degree of covalency (~88%) in Si-C bonds [6-7].

Generally, a high temperature of over 2,200°C and pressurization conditions are required to sinter fully densified SiC ceramics, whereas the TRISO-SiC fuel pellet is required a low sintering temperature of less than 1,950°C due to the decomposition of UN kernel material in TRISO particle. Therefore, the fabrication of TRISO-SiC fuel pellet necessitates the addition of a sintering aid for densification and can be sintered at a relatively low temperature using additives. The additives react with SiO₂ on the surface of SiC starting powders to form a liquid phase during sintering, which causes rapid diffusion and particle growth, enabling sintering at relatively low temperatures. The liquid phase formed is located at grain boundaries and junctions of SiC ceramics, thus changes the microstructure and affecting the properties of SiC ceramics.

KNF has been conducting a study to apply TRISO-SiC fuel pellet to light water reactor type nuclear power plant as a long-term accident tolerant fuel (ATF).

For application of TRISO-SiC fuel pellet to light water reactor fuels, the high temperature oxidation of the TRISO-SiC fuel pellet is one of important factors for safety. In addition, since the SiC matrix of TRISO-SiC fuel pellet acts as first barrier to steam if the fuel cladding is breached, the study of the oxidation behavior of liquid phase sintered (LPS) SiC is a very interesting topic.

This study investigated the oxidation behavior of LPS-SiC with sintering additives under high temperature and steam conditions as BDBA.

2. Experimental Procedure

Commercially available β-SiC powder (0.5 μm in diameter, 99.9%, Grade BF-17, H. C. Starck, Berlin, Germany), Al₂O₃ powder (0.3 μm in diameter, 99.99%, AKP-30, Sumitomo Chemical Co., Ltd., Tokyo, Japan), Y₂O₃ powder (0.4 μm in diameter, 99.99%, Kojundo Chemical Lab Co., Ltd., Sakado-shi, Japan), AlN powder (Grade F, Tokuyama Soda Co., Ltd., Tokyo, Japan), CaCO₃ powder (99% up, High Purity Chemicals, Japan) were used as the starting powders. Three batches of powder mixtures were prepared by ball milling using SiC media in a polypropylene jar for 24 hr in ethanol. The mixture of the raw materials consist of β-SiC powder and various additives of 3 wt%. The mixture was dried, sieved (60 mesh), and sintered at 1,900°C for 2 hr under an applied pressure of 40 MPa in argon atmosphere. The relative density of the sintered specimen was determined using the Archimedes method.

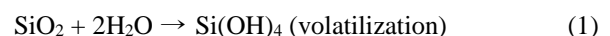
High temperature oxidation resistance of the sintered specimens was tested using tube furnace from 1,700°C for 6~50 hr with 100% steam. The steam flow speed is 200 cm/s during the tests.

The sintered specimens were polished and etched with CF₄ plasma containing 10% oxygen. The morphology of the etched microstructure was examined by scanning electron microscopy.

3. Results

The relative densities of the all hot-pressed specimens were > 99% for all samples.

During high temperature and steam oxidation test, the LPS-SiC surface is oxidized to SiO₂ causing mass loss according to the following chemical reaction equation (Eq 1.).



If mass loss condition is maintained, the liquid phase of LPS-SiC caused by the additive to SiC continues to react with SiO₂, thereby accelerating oxidation. After high temperature oxidation, typical cross section of LPS-SiC specimens is shown in Fig. 1. Exposure to the oxidation condition of LPS-SiC specimens resulted in

the formation of a porous channel on the specimen surfaces.

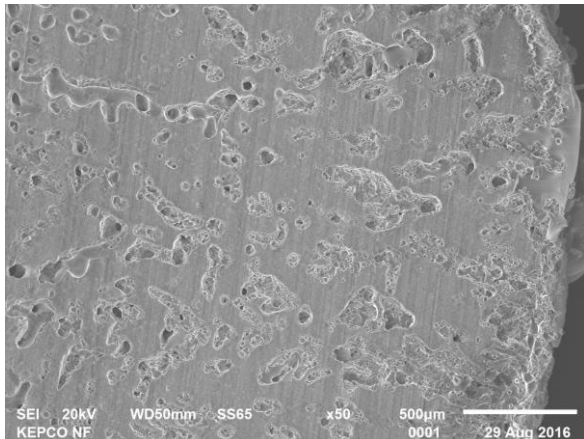


Fig. 1. Cross section after 50 hr oxidation of 3AYC specimen.

The typical microstructure of the LPS-SiC specimens is shown in Fig. 2. Liquid phase caused by the additive to SiC was found to increase with the amount of liquid phase and accelerate erosion by separating and dissolving small grains from matrix.

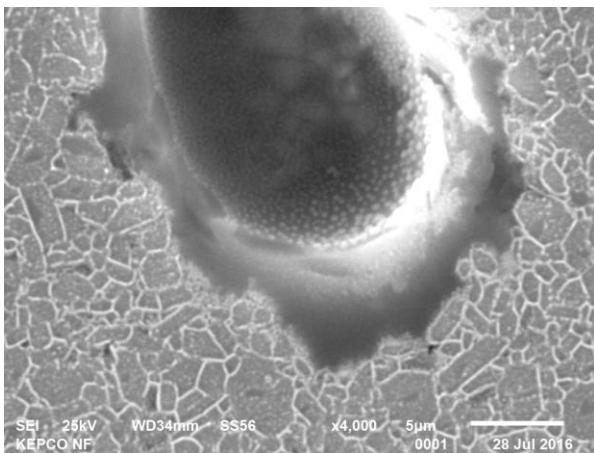


Fig. 2. Typical microstructure after oxidation of 3AYC specimen.

When LPS-SiC was applied to matrix, 30 vol% TRISO-SiC fuel pellet exposed the kernel of TRISO near the surface under oxidation conditions for 25 hr, resulting in failure to maintain its integrity. Detailed data and images on the oxidation of the SiC ceramics will be presented.

4. Conclusions

SiC ceramics with various additives of 3 wt% could be fully densified by conventional sintering at 1,900°C for 2 hr under an applied pressure of 40 MPa in argon

atmosphere. Under high temperature and steam conditions such as BDBA, the sintered LPS-SiC with additives showed the mass loss of SiC and the continuous erosion of liquid phase to form a porous channel. This oxidation behavior of LPS-SiC affects the soundness of TRISO-SiC fuel pellet. Further research is necessary to prevent oxidation.

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