
Corrosion Behavior of Fully Ceramic Micro-encapsulated Fuel during High Temperature Steam Exposure

Kwang-Young Lim¹, Yeon-Soo Na¹, Seung-Jae Lee¹, and Young-Wook Kim²

¹Materials Development Section, KEPCO Nuclear Fuel, Daejeon 305-353, Republic of Korea

²Department of Materials Science and Engineering, The University of Seoul, Seoul 130-743, Republic of Korea

ABSTRACT: *Enhancing the accident tolerance of fuels compared to the UO₂-Zircaloy nuclear fuel system has attracted a lot of interest in terms of nuclear fuel materials research and various accident tolerance fuel concepts have been proposed. Most of all, the fully ceramic micro-encapsulated (FCM) fuel concept is a reliable strategy for overcoming accident tolerance issue by multiple Silicon carbide (SiC) barriers such as SiC layer in TRISO and the dense SiC matrix of the ceramic capsules. SiC ceramics can be used under more extreme conditions owing to its enhanced oxidation resistance performance from steam reactions at high temperatures as compared to current UO₂-Zircaloy fuel systems. In this work, the high temperature oxidation behavior of FCM fuel in steam flow condition was investigated. High temperature oxidation test performed at ~1700 °C for ~50 hr with steam flow conditions. TRISO kernel located on the surface of FCM fuel began to be exposed after 25 hr. The high temperature oxidation resistance of FCM fuel was dependent on the chemistry of the additive composition for SiC matrix. Also, the grain boundary structure for SiC matrix has a significant impact on the oxidation protection of FCM fuel during high temperature steam exposure.*

KEYWORDS: ATF, SiC, FCM, Oxidation, High temperature, TRISO

I. INTRODUCTION

The recent events at the Fukushima Daiichi nuclear power plant in Japan highlighted the need for added safeguard, including fuels with enhanced accident tolerance that can delay or even prevent severe accidents. Therefore, enhancing the accident tolerance of the nuclear fuels than UO₂-Zircaloy fuel system has attracted a lot of interest in terms of nuclear fuel materials research and various accident tolerance fuel (ATF) concepts have been proposed. SiC received considerable attention for ATF material and nuclear power applications due to low neutron cross section, radiation stability, high thermal conductivity, superior high thermal stability, chemical inertness, and excellent resistance to oxidation [1-6]. Especially, the FCM fuel concept is a reliable strategy for overcoming accident tolerance issue due to its a potential for achieving higher safety margins under beyond-design-basis accident (BDBA) scenarios by multiple SiC barriers such as SiC layer in TRISO and the dense SiC matrix of the ceramic capsules. The performance on high temperature oxidation of FCM fuel is one of important factors for plant safety of nuclear reactors and given the significant interest in SiC material for the FCM fuel, the high temperature oxidation of SiC has received considerable attention. Usually, SiC ceramic matrix for FCM fuel was fabricated by liquid phase sintering (LPS) method with additive system. Thus, investigating of corrosion behavior on SiC matrix of FCM fuel during high temperature steam condition exposure as BDBA condition is highly interesting.

II. EXPERIMENTAL PROCEDURE

Monolithic SiC and FCM fuel (40 vol% TRISO) were prepared by powder mixtures. The powder mixtures of the raw materials were β -SiC and ~5 vol% various additives. The mixtures and mixture overcoated TRISO particles were hot-pressed at 1875°C for 2 hr under 15 MPa in an argon atmosphere, respectively.

The weight change by oxidation was measured using thermogravimetry (TGA, Netzsch STA 449 F3) from 200 °C to 1200 °C for 50 hr with ~68% steam-Ar. The water injection rate was ~2.5 mL/h during the tests. Also, high temperature oxidation resistance was performed 1700 °C for 25~50 hr with 100% steam. The water injection rate was 15 mL/min during

the tests. After oxidation, the 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., Japan).

III. RESULTS

III.A. Effect of Additives on Weight Changes of LPS-SiC Ceramics during Steam Oxidation at 1200°C

The weight changes of monolithic SiC specimens at 1200 °C were increased with increasing additive content and dependent on the chemistry of the additive composition. The SiC ceramics sintered with alumina-yttria-calcia (AYC) additives exhibited the minimum weight change of $\sim 0.45 \text{ mg/cm}^2$ at 1200°C for 50hr in 68% steam-Ar among all the specimens with the additives containing Al because of the crystalline state of intergranular glassy films (IGF) in SiC ceramics with AYC additive [7] whereas usually Al containing additives form amorphous intergranular glassy films in SiC ceramics [2,8]. The diffusivity of cation through amorphous intergranular films is considered to be faster than that in crystalline intergranular films due to low viscosity of amorphous intergranular films at high temperature as 1200°C. Therefore, weight improvement by oxidation is accelerated through amorphous intergranular film and the grain boundary structure has a significant impact on the oxidation of LPS-SiC ceramics.

III.B. High Temperature Steam Oxidation Test

High temperature steam oxidation test of monolithic LPS-SiC was performed for observing corrosion behavior because primary protective barrier of FCM fuel is SiC matrix. Fig. 1 shows the cross-section of monolithic LPS-SiC ceramics after 25 hr of steam exposure at 1700 °C. After oxidation LPS-SiC specimen shows SiO_2 bubbles and corrosion on the surface of SiC. Also, cross-section of LPS-SiC specimen was observed large amount of pore channels by liquid penetration and corrosion. The penetrated pore channels depth by corrosion from the surface was about 2 mm. Although there was a difference in penetrated depth, these results were similarly observed for all LPS-SiC specimens. Also, it was confirmed that an oxide film was formed on the surface of SiC, but a liquid phase wetting phenomenon occurred locally (Fig 2). The reason of these results are as follows; 1) The SiO_2 layer formation on surface of SiC; 2) formation of liquid phase due to lowered melting temperature by reaction between additives and SiO_2 layer at junction; 3) wetting and permeating liquid phase through weak or junction part in SiC; 4) dissolving of smaller SiC grain than the critical size; 5) liquid phase continually reacts to compound at junction and grain boundary; 6) formation of pore channel and accelerating chemical reaction; 7) bubbling of liquid phase; 8) removing liquid phase by volatilization. These wetting and corrosion phenomena did not occur in solid state sintered (SSS) SiC and CVD-SiC. Therefore, LPS-SiC is more vulnerable to attack from the high temperature corrosion than the SSS-SiC and CVD-SiC due to rapid dissolution of the intergranular films by sintering additives. The SiC ceramics sintered with AYC additives showed minimum penetrated pore channels depth of about 1.2 mm from the surface due to crystalline intergranular films.

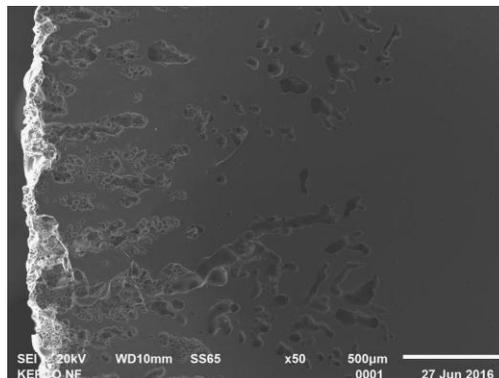


Fig. 1. The cross section of LPS-SiC pellet after high temperature steam oxidation

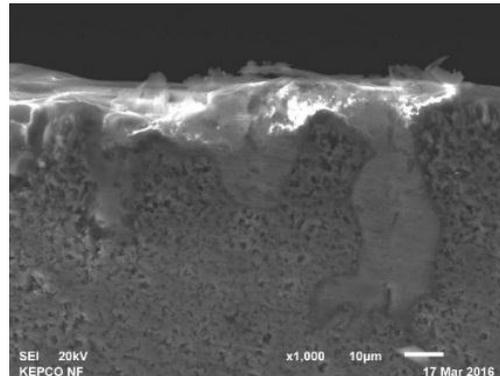


Fig. 2. The localized liquid phase wetting of LPS-SiC after high temperature steam oxidation

Fig. 3 shows corrosion boundaries of etched LPS-SiC specimen by liquid phase. The intergranular films as surrounding SiC grain must be dissolved before dissolving the SiC grain and it is needed additional SiO₂ provision by penetrated liquid phase. The dissolution of the intergranular film prefer to act on small grain that has a short diffusion path as grain boundary than large grain. Since it is easy to dissolve smaller grain than the critical size, the corrosion and liquid penetration are delayed in large grain critical size having a relatively low solubility and it is located at the grain boundary of large grains. Consequently, large grain and clean grain boundary structure of LPS-SiC have an advantage for high temperature steam oxidation.

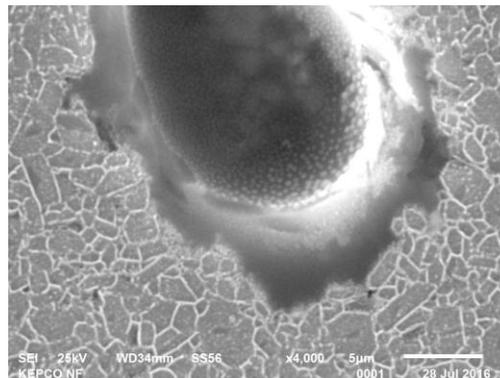


Fig. 3. The corrosion boundaries of LPS-SiC

After high temperature oxidation test to imitate BDBA for 25 hr, the shape of FCM fuel with 40 vol% TRISO particles maintained soundness and formed SiO₂ bubbles on the surface. The cross-section of FCM pellet was observed large amount of pore channels along the boundary between TRISO and SiC matrix. Liquid phase by reaction between additives and SiO₂ on the surface of SiC matrix significantly corrodes the FCM fuel regardless of additive composition and damages to TRISO particles. Nevertheless, TRISO kernels were not exposed by protection SiC layer on the TRISO particles and thickness of damaged SiC layer on TRISO particles was on the order of several microns. Therefore, it is expected that TRISO kernel located on the surface of FCM fuel began to be exposed after about 25 hr.

Fig. 4 shows the cross section of FCM fuel (40 vol% TRISO) after high temperature steam oxidation for 50 hr. TRISO kernels of FCM fuel were some exposed and limited to some surface area. However, about half of exposed TRISO particle was protected by SiC layer and the mostly TRISO was protected. After high temperature oxidation test, the shape of FCM fuel maintained whereas the outside of FCM fuel was partially broken during machining due to strength degradation of porous SiC matrix by pore channels. The FCM fuel showed penetrated pore channels depth of about 2.5 mm from the surface and located TRISO kernels under 500 µm from the outside of SiC matrix were mostly protected by SiC layer on the TRISO particles. These results indicate that FCM fuel has excellent safety performance in terms of accident tolerance.

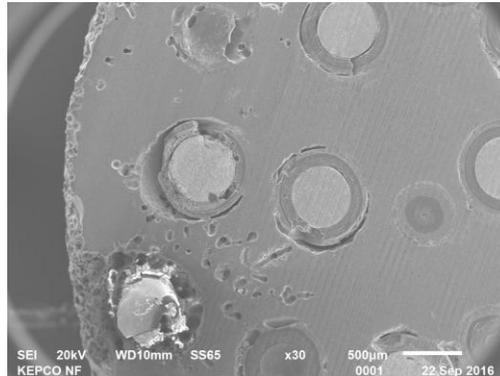


Fig. 4. The cross section of FCM fuel with 40vol% TRISO after high temperature steam oxidation for 50 hr

IV. CONCLUSIONS

Monolithic SiC and FCM fuel (40 vol% TRISO) with various additives were fabricated by hot-pressing method and performed high temperature oxidation test at ~ 1700 °C for ~ 50 hr with steam flow conditions. LPS-SiC showed SiO₂ bubbles and corrosion on the surface of SiC. The corrosion of SiC by liquid phase is dependent on the grain size and additive composition. The AYC additive composition for FCM matrix showed the best high temperature steam oxidation resistance performance than the other compositions due to completely crystallized intergranular films and ternary junctions. In case of LPS-SiC for FCM fuel, large grain and clean grain boundary structure have an advantage for high temperature steam oxidation. Finally, TRISO kernel located on the surface of FCM fuel began to be exposed after about 25 hr. After high temperature steam oxidation for 50 hr, TRISO kernels of FCM fuel were some exposed. However, exposure of the TRISO kernel was limited to some surface area and the mostly TRISO was protected, indicating excellent safety performance of FCM fuel.

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