Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Microstructure and hydrothermal corrosion behavior of NITE-SiC with various sintering additives in LWR coolant environments☆

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ARTICLE INFO

Article history:
Received 22 September 2016
Accepted 22 November 2016
Available online xxx

Keywords:
Silicon carbide
Liquid phase sintering
Sintering aid
Hydrothermal corrosion
Light water reactor
Scanning transmission electron microscopy
Multivariate statistical analysis

ABSTRACT

Nano-infiltration and transient eutectic phase (NITE) sintering was developed for fabrication of nuclear grade SiC composites. We produced monolithic SiC ceramics using NITE sintering, as candidates for accident-tolerant fuels in light-water reactors (LWRs). In this work, we exposed three different NITE chemistries (yttria-alumina [YA], ceria-zirconia-alumina [CZA], and yttria-zirconia-alumina [YZA]) to autoclave conditions simulating LWR coolant loops. The YZA was most corrosion resistant, followed by CZA, with YA being worst. High-resolution elemental analysis using scanning transmission electron microscopy (STEM) X-ray mapping combined with multivariate statistical analysis (MVSA) datamining helped explain the differences in corrosion. YA-NITE lost all Al from the corroded region and the ytttria reformed into blocky precipitates. The CZA material lost all Al from the corroded area, and the YZA – which suffered the least corrosion –retained some Al in the corroded region. The results indicate that the YZA-NITE SiC is most resistant to hydrothermal corrosion in the LWR environment.

1. Introduction

Advanced materials have the potential to enhance the performance, reliability, and safety of the current fleet of nuclear power plants as well as many advanced platforms under development today [1,2]. A specific example is the development of accident-tolerant fuel and cladding materials to replace the urania/Zr-based alloy fuel system in light water reactors (LWRs) [3]. SiC-based materials are particularly well suited for this purpose since they exhibit exceptional radiation tolerance [4,5] as well as high temperature steam oxidation resistance [6,7]. Accordingly, utilization of SiC-based materials has been proposed both in the form of fuel cladding, as well as in the fuel pellet itself. The former takes advantage of the well-established SiC fiber/SiC ceramic matrix composite (SiC/SiC) technology to produce a tough cladding material [8–12]. The specific manifestation of the fuel pellet is the fully-ceramic-microencapsulated fuel (FCM) [13,14], where tristructural isotropic (TRISO) fuel kernels are embedded inside a sintered SiC matrix. To achieve sufficiently low processing temperatures for the sintered SiC matrix to avoid damaging the TRISO fuel kernels, the nano-infiltration by transient eutectic (NITE) process [15–18] is used. The NITE process is a special type of the conventional liquid phase sintering (LPS) process [19–21] where small amounts (preferably <10 wt% and as low as ~3 wt%) of oxide additives are added to SiC nanopowder as sintering aids. Utilization of the nanopowders tends to reduce the amount of oxide additives needed for full densification, but may increase the consolidation temperature [17,22]. The oxide additives are generally a mixture of alumina, silica and rare earth oxides (usually yttria) blended at eutectic ratios to form a liquid phase during sintering. The NITE sintering process is remarkable in that by utilizing SiC nanopowder on the order of tens of nanometers in diameter it results in a dense SiC structure after consolidation at <1900 °C in which the SiC grains (usually 3C β-phase) are on the order of a few micrometers. The grain boundaries are wet by thin films (~2 nm) of the amorphous oxides. Further, at SiC-grain triple-points, there are often larger pockets of the oxides (tens or hundreds of nm). These oxide pockets will sometimes be crystalline, and sometimes be amorphous. In previous work on Y_2O_3-Al_2O_3 added NITE SiC, for instance, Al-Y-O rich grain

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http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.033
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Please cite this article in press as: C.M. Parish, et al., Microstructure and hydrothermal corrosion behavior of NITE-SiC with various sintering additives in LWR coolant environments, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.033

boundary films, Al-Y-O triple-points, and Al-O only (Y-deficient) triple-points were observed [23]. Both amorphous and crystalline phases were noted. Even more remarkable is that the transition appeared to result in differential swelling compression of the grain boundaries, resulting in increased strength after irradiation. [24].

For ultimate deployment of SiC-based materials as nuclear fuel or cladding, a number of engineering issues must be explored and quantified [25,26]. In this paper, we explore the question of hydrothermal corrosion of the NITE-SiC in LWR coolant environments under normal operating conditions. Due to differences in aqueous parameters such as oxygen activity, corrosion performance is expected to depend on the specific water chemistry in PWR (pressurized water reactor) and BWR (boiling water reactor) coolant environments. Monolithic SiC (such as chemical vapor deposited [CVD]) SiC shows corrosion resistance superior to sintered SiC variants [27–29]. Previously it was shown for high-purity SiC variants (i.e. CVD-SiC), the corrosion proceeds initially via oxidation of Si and C by the water molecule and subsequent dissolution of silica in water where the rate limiting step is the oxidation of Si [30]. Since the oxidation reaction is the rate limiting step, reducing the oxygen activity in the aqueous environment reduces the rate of material recession [30,31]. Even for the high purity variants, the grain boundaries, largely free of any impurities, were identified as active corrosion/dissolution sites [32,33]. Grain boundary corrosion was shown to highly accelerate for sintered variants [27], likely due to rapid dissolution of the intergranular sintering additives.

In this study, the corrosion behavior of the standard NITE-SiC with yttria-alumina sintering additives was examined in three distinct LWR water chemistries. In parallel, a corrosion rate of the major sintering additive, alumina, was studied in separate tests. After observation of the rapid dissolution of alumina in various LWR coolant environments, an effort was undertaken to produce novel NITE-SiC variants with significantly reduced alumina contents. Instead, oxide additives with negligible aqueous corrosion rates were meant to be used as sintering aids. The corrosion behavior and microstructure (before and after corrosion test) of all these NITE variants are reported in this study. Specifically, advanced analytical scanning transmission electron microscope (STEM) techniques were used to produce large area, high-count-rate X-ray maps in order to determine the local nanochemistry in the grains, on the grain boundaries, and at the triple-points. Computational datamining via multivariate statistical analysis (MVSA) of the X-ray maps was used to find correlations between the cations, and MVSA discovered unexpected elemental species.

2. Procedure

2.1. Fabrication of materials

The NITE-SiC materials were all produced at ORNL with detailed descriptions of the fabrication procedure in previous publications [17,22]. Briefly, SiC nanopowder was milled along with oxide additives using Si_3N_4 media in ethanol. Two distinct SiC nanopowders with 40 and 80 nm average particle size were used with purity of 99% and >99%, respectively (supplied by Nanostructured & Amorphous Materials, Inc., China and Nanomakers, France, respectively). The densification was achieved by hot pressing the powders inside a graphite die under Ar at 1875 °C for 1 h at 10 MPa.

This study intended to investigate the effect of various oxide sintering additives on corrosion behavior of NITE-SiC. The reference NITE material was produced using alumina and yttria mixed at the composition corresponding to their lowest temperature eutectic, henceforth referred to as YA-NITE. This is by far the most utilized system for production of sintered SiC with oxide additives. As discussed in the next sections, one of the goals of this study was to eliminate alumina in the mix of sintering additives. Also, it was intended to include zirconia as a sintering additive because zirconia exhibits exceptional radiation stability [34] and negligible dissolution in aqueous environments [35]. The latter is clearly evident from the experience with irradiation of tens of millions of Zr-based alloy cladding tubes in LWR coolant environments where there was no or negligible dissolution of the zirconium oxide film that forms of the surface of these alloys. To ensure radiation stability of zirconia phase, it was intended to stabilize the fluorite structure by addition of yttria or ceria in the mix [36]. The challenge with incorporation of zirconia into the mix of oxide additives without inclusion of alumina is melting it to form the liquid phase. Although silica forms a eutectic with zirconia at temperatures below the maximum processing temperatures of interest, it is a very silica rich liquid [37]. This means that a large amount of silica is needed to melt a small amount of zirconia, and bodes ill with the goal of limiting oxide additives in the system. The binary phase diagrams make it clear that addition of yttria and ceria alone will not result in a liquid phase formation with zirconia [38,39]. Therefore, the adopted strategy was to add only a small amount of alumina compared to the reference YA-NITE specimen.

Table 1
Oxide additive content in the feedstock and the resulting density after hot-pressing for various NITE-SiC specimens.

NITE-SiC	Feedstock oxide additive content in wt%				Density
ID	ZrO_2	Y_2O_3	CeO_2	Al_2O_3	g/cm^3
YA		2.9		3.1	3.09
CZT-1	3		4	0	2.51
CZT-2	3		4	0.25	3.03
CZT-3	3		4	0.375	3.11
CZT-4	3		4	0.5	3.24
CZA-1	3		4	0.45	3.21
CZA-2	4		2	0.45	3.21
YZA	4	2		0.45	3.24

Table 2
Summary of autoclave conditions for immersion tests. PWR: pressurized water reactor. BWR: boiling water reactor. HWC: high water chemistry. NWC: neutral water chemistry.

Autoclave	Chemistry	Temperature (°C)	pH	Pressure (MPa)
PWR	3.57 ppm H_2	330	7.2	15
BWR-HWC	0.3 ppm H_2	290	5.6	7
BWR-NWC	1.0 ppm O_2	290	5.6	7

Table 1 denotes the nominal composition of the powder feedstock (essentially the mixing recipe) as it was initially milled, and the resulting densities. The YA specimen was the reference material with yttria-alumina sintering aids. The CZT series of specimens were small batch (~10 g) materials prepared and hot-pressed to determine the minimum amount of alumina needed to achieve a dense specimen. As evident from the table, as alumina content increased, the density of the sintered specimen improved significantly. Based on this information, the alumina content of 0.45 wt% was used to prepare large batch (~100 g) feedstock for plate production of zirconia bearing NITE-SiC specimens. CZA-1, CZA-2, ad YZA plates were produced accordingly to examine the effect of ceria, zirconia, and yttria content on microstructure and hydrothermal corrosion behavior.

2.2. Hydrothermal corrosion testing

Details of hydrothermal corrosion test conditions have been previously described [30]. The test conditions are summarized in Table 2. Briefly, the tests were conducted in flowing autoclave loops at GE Global Research Center (Schenectady, NY) with strict control of water chemistry. The tests for the different specimens were