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Corrosion behavior of ZrC–SiC composite ceramics in LiF–NaF–KF molten salt at high temperatures

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Abstract

The suitability of ZrC–SiC-based ceramics was assessed as candidate materials for fluoride. An immersion corrosion with ZrC–SiC composites was performed in molten FLiNaK salts (LiF–NaF–KF: 46.5/11.5/42 mol%) at 850 °C. Results indicated that ZrC–SiC-based ceramics were more corrosion resistant than the ZrC ceramic. ZrC–40SiC ceramic exhibited 50% weight-loss to ZrC. This carbide exhibited minimal corrosion attack because of strong resistance to dissolution in molten fluorides. Furthermore, XRD results were consistent with weight-loss and SEM results. The corrosion behavior of ZrC–SiC-based ceramics was affected by impurities, particularly oxygen content. Oxygen and/or oxygen ion participated in corrosion of ceramic. Corrosion of carbide ceramics is mainly due to C^{4-} in ceramics. This ion is oxidized to elemental C by oxidants or impurities in the molten salt. The addition of C may inhibit corrosion of molten salts and thus improve the corrosion resistance of carbide ceramics.

Keywords: C. Corrosion; Silicon carbide; Zirconium carbide; Molten FLiNaK salts; Micromorphology

1. Introduction

Zirconium carbide (ZrC) possesses high melting temperature, high fracture strength, high electrical and thermal conductivities, and resistance to erosion/corrosion [1]. ZrC is a candidate material for reactors because of its excellent neutronic properties [2]. However, the poor chemical stability of ZrC at high temperatures in oxidizing atmosphere significantly limits its actual application [1,2]. A common approach to improve oxidation resistance is by incorporating Si-containing compounds into the ZrC matrix to form a protective SiO_2-containing oxide scale [3–5]. Zhao et al. prepared composites comprising ZrC and 30 vol% silicon carbide (SiC) [4]. The protective effect of the oxide scales is enhanced by the formed SiO_2 [4]. ZrC–SiC composites can generate high-performance ceramics; these composites demonstrate the passivating characteristic of SiC and the high melting temperature, hardness, and thermal stability of ZrC [3–5]. ZrC–SiC composites are broadly applied under extreme conditions and can be potentially use in fluoride salts because of their good thermo-mechanical properties, irradiation resistance, and chemical stability at high temperatures [2,6,7]. ZrC–SiC composites are suitable candidate materials in molten salt environments.

The molten LiF–KF–NaF eutectic salt (46.5/11.5/42 mol%), commonly referred as FLiNaK, is a leading candidate material for heat transfer fluids because of its superior heat transfer properties [8,9]. FLiNaK molten salts can be used as a secondary coolant and a primary simulation coolant in molten

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salt reactors (MSRs) [10,11]. FLiNaK molten salts can also be used as a primary coolant in advanced high-temperature reactors [12,13]. FLiNaK salts are used in MSRs because of their high thermal conductivities, high specific heats, low viscosities, and high boiling points. However, FLiNaK molten salts can be corrosive to materials at high temperatures; corrosion resistance under high-temperature environments is compromised by the thermodynamic instability of the protective oxide layer [14–16]. Ceramics exhibit excellent properties, such as high melting point, hardness, strength, and chemical stability. These attractive characteristics result in broad application of ceramics under extreme conditions. Ceramics are unique candidate materials that can be used at high temperatures (approximately 1000 °C) for a long time and satisfy the requirements of Generation IV nuclear reactors [17]. Related research work has been performed but cannot support the requirements to be classified as Generation IV nuclear reactors. Nishimura dipped SiC in an LiF–BeF_2 (66/34 mol%) solution with traces of HF at 550 °C; after 10 days, a thick deposit with a depth of 500 nm was obtained, which exhibits very good fluoride corrosion resistance [18]. Schmidt and Peterson immersed SiC in FLiNaK molten salt at 850 °C to improve its corrosion resistance [19]. However, limited work has been conducted with regard to the corrosion of ZrC and ZrC–SiC composites in FLiNaK molten fluorides. The compatibility of fresh molten salts with materials is a technology gap for heat transfer applications; such materials derive their corrosion resistance from the formation of a protective surface oxide film, which is chemically unstable in most high-temperature fluoride salts. MSR materials are severely challenged by high operating temperatures and corrosive environments of molten fluoride salts; in particular, these materials are corroded in high-temperature molten fluorides.

In this study, the static corrosion behavior of ZrC and ZrC–SiC-based ceramics dipped in FLiNaK molten salts is determined. The corrosion behavior and compatibility of ZrC–SiC-based ceramics with the FLiNaK molten salt mixture were elucidated. With thermodynamics as the basis, microstructural analysis and X-ray diffraction (XRD) were employed to explain the possible corrosion mechanism. Some interesting phenomena were reported which have not been found in previous works.

2. Materials and methods

2.1. Materials

ZrC ($>99\%$ purity, 1.0 μm) and SiC ($>99\%$ purity, 0.45 μm, Changle Xinyuan Carborundum Co., Ltd., China) starting powders were used; ZrC was synthesized through carbothermal reduction as described in a previous work [1,5]. ZrC, ZrC with different SiC contents (20 and 40 vol%), and SiC with 2.0 wt% B_4C and 1.0 wt% C additives were mixed with ethanol in a plastic bottle through ball mixing of Si_3N_4 for 24 h; the corresponding samples were designated as ZrC, ZrC–20SiC, ZrC–40SiC, and SiC. A rotary evaporator was used to remove ethanol at 70 °C. The powder mixtures were sieved through a 200 mesh. The obtained mixed powders were hot pressed at 2100 °C. A pressure of 30 MPa was applied at 1450 °C to produce a rectangular sample with dimensions of 37 mm (length) × 30 mm (width) × 5 mm (height). The atmosphere was vacuum (<10 Pa) at 1000 °C and then switched to flowing argon (99.99% pure). A detailed description of the experimental materials and processes can be found in the literature [1]. The bulk densities of sintered ceramics were measured using the Archimedes method. Final relative densities were determined as the ratio of the experimental bulk densities to the theoretical densities calculated using the rule of mixtures. The final relative densities of ZrC, ZrC–20SiC, ZrC–40SiC, and SiC were 99.0%, 99.2%, 98.8%, and 98.6%, respectively.

FLiNaK salt was purified with NH_4HF at 750 °C under vacuum. In this purification process, residual water and oxygen were removed from the melt and metal impurities were minimized. The salt sample was analyzed using inductively coupled plasma–optical emission spectrometer (ICP–OES) before detecting the following impurities: 11 ppm Ca, 10 ppm Ni, 7 ppm Mg, and 101 ppm Si. Other elements were determined below 5 ppm or below the quantitative detection limits of ICP–OES. The impurities present in FLiNaK can significantly affect the corrosion behavior. For example, water present in the initial salt can significantly induce corrosion by producing HF. In the present study, the effects of trace impurities on corrosion were not specifically investigated to compare the relative corrosion performance of various materials. The concentrations of residual oxygen and water in FLiNaK were 1150 and 150 ppm as determined through a LECO oxygen analyzer and Karl–Fischer titration, respectively. The eutectic was then crushed into powder and stored in a glove box with argon gas.

Test coupons were nominally cut into 12.5 mm (length) × 10.0 mm (width) × 3.0 mm (height) by using a wire-cut electrical discharge machine. The coupons were progressively ground with a 320-grit SiC sand paper and then with 1200-grit SiC. The coupons were finally polished using 1-μm diamond paste. After mechanical grinding, the coupons were degreased in an ultrasonic bath of acetone and alcohol for 5 min and then rinsed in deionized water before testing.

2.2. Corrosion procedure

A schematic drawing of the experimental apparatus is shown in Fig. 1. The following procedures were performed in this apparatus. Three samples of a given test ceramic were fixed at each groove of graphite rods. The rods were placed in their corresponding graphite crucibles and then baked at 750 °C in an Ar environment for 8 h. All samples were tested in triplicates, with one crucible assigned to each ceramic. A schematic illustration of the design is shown in Fig. 1(b). The crucibles were filled with 50.0 g of FLiNaK salt before transferring to a furnace, where they were heated and maintained at 850 °C. After 100 h of exposure, the furnace temperature was decreased to room temperature and the FLiNaK salt was removed from the experimental apparatus.