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Corrosion behavior of TiC–SiC composite ceramics in molten FLiNaK salt

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ABSTRACT

Immersion corrosion tests of $TiC_{0.8}$, TiC, TiC–20 vol% SiC, TiC–40 vol% SiC and SiC have been performed in molten FLiNaK salt at 800 °C for 25–200 h under argon cover gas. All of these five samples showed small mass loss and relatively good corrosion resistance in molten FLiNaK salt. The corrosion patterns of $TiC_{0.8}$, TiC, TiC–20 vol% SiC and TiC–40 vol% SiC were inter-granular corrosion, which were attributed to the depletion of Ti along the grain boundaries. SiC exhibited a general corrosion process in which a carbon-rich layer formed on the surface, resulting from the depletion of Si. The carbon-rich layer protected SiC against further corrosion, hence lowering the corrosion rate. The corrosion results of TiC–20% SiC and TiC–40% SiC revealed the corrosion resistance of TiC could be improved by adding SiC. And the contribution of SiC to better corrosion resistance has been elucidated.

1. Introduction

Molten salt reactor (MSR) has been selected as one of the six promising Gen-IV nuclear reactors [1]. Molten FLiNaK salt (46.5 mol% LiF, 11.5 mol% NaF and 42 mol% KF, eutectic point 454 °C) is a promising candidate material for use as primary reactor coolants and heat transfer media due to its desirable properties including good thermal conductivity (0.82–0.96 W/m·K at 800–1100 K), high specific heat (1.82–2.14 J/g·K at 800–1100 K), low viscosity (1.95 mPa·s at 800 °C) and high boiling point (1843 K) [2–4]. However, molten FLiNaK salt can be corrosive to materials at high temperatures. Thus, the development of materials with high corrosion resistance in molten FLiNaK salt has been an important issue. So far, great efforts have been devoted to the study of corrosion behavior of different materials in molten fluoride salts. Previous works proved that most oxide films, which usually could prevent further oxidation of materials, were chemically unstable in molten fluorides. For alloys, the corrosion was mainly attributed to the dissolution of alloying elements into molten salt. Olson et al. [5] and Wang et al. [6] proved that corrosion of Ni based alloys proceeded predominantly by dealloying of Cr. The impurities in molten salts such as H_2O and oxides expedited the corrosion process. Quyang et al. [7] showed that Ni-alloys in the FLiNaK salt with higher moisture content suffered from more serious corrosion, which should be attributed to the attacks of hydrogen fluoride (HF, generated by the reactions between impurities and molten salt).

Some ceramics also could be alternative promising materials used in MSR due to their excellent properties, such as high melting point, strength and chemical stability. According to the experiments performed at Oak Ridge National Laboratory, SiC showed no noticeable attacks in molten FLiNaK at 700 °C [8]. He et al. [9] reported that SiC could be an alternative for the protection of nuclear graphite from liquid fluorides since it could be against the permeation of molten fluoride salts. But the oxygen impurity in SiC weakened its corrosion resistance [10]. Thus high purity SiC is particularly required. The corrosion behavior of other candidate

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ceramics, such as ZrC [11], also has been investigated. Zr was found to be selectively corroded from ZrC. ZrC showed poor corrosion resistance while the addition of SiC could reduce the weight loss of ZrC in molten FLiNaK salt.

Besides SiC and ZrC, titanium carbide (TiC) is also an important candidate ceramic material for applications in nuclear reactors because of high melting point (>3000 °C), good thermal conductivity, low permeation of tritium and excellent radiation resistance [12–14]. Moreover, TiC has good chemical stability. TiC coating has been synthesized in KCl–LiCl [15], NaF–NaCl [16] and LiCl–KCl–KF [17] molten salts at high temperatures, which suggests TiC is stable in various molten salts. Similarly, the fact that two-dimensional Ti_3C_2 (a member of the 'MXene' family) [18,19], which was produced by etching aluminum from Ti_3AlC_2 in concentrated hydrofluoric acid, also indicated that non-stoichiometric TiC had good corrosion resistance to HF. These results inferred that TiC is likely to have good performance in FLiNaK salt at high temperatures. However, few works has been conducted to regard the corrosion resistance of TiC in molten FLiNaK salt.

In this study, the static corrosion behaviors of TiC and $TiC_{0.8}$ in molten FLiNaK salt have been studied. Since SiC was usually used as reinforcement in ceramic composites [20,21] and itself showed good anticorrosion property, TiC–SiC composites have also been synthesized and dipped in molten FLiNaK salt to investigate their corrosion performance. Finally, the different corrosion characteristics and the possible corrosion mechanisms have been discussed.

2. Materials and methods

2.1. Materials

The raw powders were TiC (SICCAS, China, purity > 99%, mean diameter ~ 0.56 μm), SiC (Changle Xinyuan Carborundum Co., Ltd., China, purity > 99%, mean diameter ~0.45 μm,) and titanium powders (Shanxi Fengxiang Co. Ltd., China, purity > 99%, mean diameter ~1–2 μm). Near fully dense (relative density > 99%) $TiC_{0.8}$, TiC, TiC–20 vol% SiC (named as TiC–20SiC), TiC–40 vol% SiC (TiC–40SiC) and SiC (added with 0.5 wt% B_4C) ceramics were fabricated by the following procedure. The raw mixtures were ball-milled (Si_3N_4 balls) in ethanol at a speed of 300 rpm for 5 h. The slurry was dried at 60 °C in a rotary evaporator and sieved through a 200-mesh screen. Then, the powder mixtures were placed in a graphite die and hot-pressed in a graphite furnace (ZT-60-22Y, Chen Hua Electric Furnace Co. Ltd., China). To minimize oxygen content, the samples were heated to 1600 °C (<10 Pa) with a heating rate of 10 °C/min and hold for 30 min. Then a pressure (30 MPa) was applied and the furnace atmosphere was changed from vacuum to following argon ($>10^5$ Pa, purity > 99.9%). Subsequently, the samples were heated to 2000 °C at the same rate and hold for 1 h. After sintering, the applied pressure was removed and the furnace was cooled to room temperature naturally. The as-synthesized bulk ceramics ($37 \times 30 \times 8\,mm^3$) were cut into small pieces and all surfaces were polished. Final test samples have dimensions of $10 \times 8 \times 3\,mm^3$. Oxygen content in ceramics was determined by a nitrogen/oxygen determinator (TC600, Leco Corporation, USA), which were $TiC_{0.8}$ (0.79 wt%), TiC (0.68 wt%), TiC–20SiC (0.72 wt%), TiC–40SiC (0.74 wt%) and SiC (0.24 wt%), respectively. FLiNaK salt was provided by Shanghai Institute of Applied Physics, Chinese Academy of Sciences. The main impurities in salt are presented in Table 1.

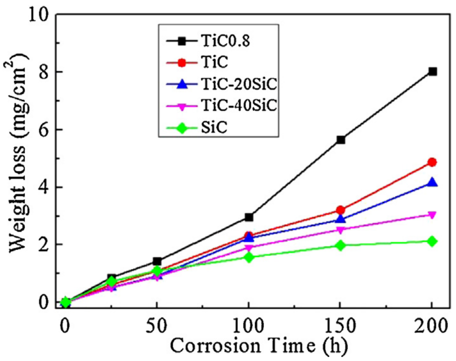

Fig. 1. Results of weight loss of samples after different periods of corrosion tests.

2.2. Corrosion procedure

Before experiments, all samples were washed with acetone, alcohol and deionized water to clean the surfaces. Then, ceramic bulks and 20 g FLiNaK salt were encapsulated in graphite crucible by glove box filled with Ar gas. Afterwards, the sealed graphite crucible with samples was maintained at 800 °C in a furnace (under flowing argon, purity > 99.9%) for 25, 50, 100, 150 and 200 h, respectively. After corrosion experiments, samples were cleaned of FLiNaK salt by using aluminum nitrate, acetone, alcohol and deionized water according to the method used in previous works [7,10,11]. Phase compositions were investigated via X-ray diffraction (XRD, D/Max-2250 V, Rigaku, Japan) and Laser Micro-Raman Spectrometer (DXR, Thermo Fisher Scientific, USA). To maintain the structural integrity of samples, some cross sections were prepared by argon ion-beam polishing (EM TIC 3X, Leica, Germany), using an accelerating voltage of 7 kV for 5 h. The ion beam impinged on the edge of a corroded surface, producing a semicircular flat surface on the cross section as described elsewhere [22]. Microstructures were analyzed by a SEM system (Magellan 400, FEI, USA) equipped with EDS (INCA SERIES, Oxford Instrument, UK).

3. Results and discussion

3.1. Mass changes

The changes in weight of ceramics corroded at 800 °C for different times are presented in Fig. 1.The weight loss of $TiC_{0.8}$, TiC, TiC–20SiC, TiC–40SiC and SiC caused by corrosion was of negative values, all of which increased with immersion time. Among the tested ceramics, $TiC_{0.8}$ exhibited poorest corrosion resistance since it showed the maximum weight loss of about 8.04 mg/cm^2 after 200 h corrosion test, which was much larger than other four tested ceramics. TiC, TiC–20SiC, TiC–40SiC and SiC presented similar mass loss for testing durations of 0–50 h. With the corrosion time increasing, SiC tended to show minimum weight loss. Meanwhile, it can be noted that the addition of SiC could reduce the weight loss, inferring that SiC has dominant contribution to improving corrosion resistance of TiC.

3.2. Microstructural characterization

The XRD patterns of virgin and corrode samples are presented in Fig. 2. No other crystalline phases could be detected in the

Table 1
Concentration of impurities in FLiNaK salt (ppm).

Ba	Cr	Fe	Mg	Ni	Ca	Si	NO_3^-	PO_4^{3-}	SO_4^{2-}	H_2O
43.27	4.24	16.97	1.75	20.02	6.73	73.34	22.8	16.8	1.9	<10

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