



Letter to the Editor

SiC coating: An alternative for the protection of nuclear graphite from liquid fluoride salt



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ARTICLE INFO

Article history:

Received 18 December 2013

Accepted 21 January 2014

Available online 28 January 2014

ABSTRACT

SiC coating is produced on a nuclear graphite (NG) substrate using chemical vapor deposition at 1150 °C to protect it from molten salt diffusion. Infiltration studies, performed in molten FLiNaK salt under an argon atmosphere at 5 atm, show that uncoated NG exhibits significantly higher weight gain than SiC-coated NG. The continuous and compact SiC coating exhibits excellent infiltration resistance in liquid fluoride salt as confirmed by synchrotron radiation X-ray microbeam fluorescence.

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1. Introduction

Nuclear power is one of the best choices to meet future energy demands due to its advantages in fuel economy, cost-effective operation, and environmental protection. For all the six promising future reactors proposed by the Generation IV International Forum [1], molten salt reactor (MSR) has incomparable advantages: a high negative temperature coefficient of reactivity, a very low vapor pressure, thermodynamic stability, and so on [2,3]. Additionally, the waste produced in an MSR is shorter-lived than the waste produced by other reactor types by a factor of 10–100. In MSR, nuclear graphite (NG) is used as a neutron moderator and a reflector to slow down fast neutrons. Furthermore, the molten salt (a mixture of fluorides) used both as a fuel and as a coolant flows between the graphite reactor core and the heat exchanger. Notably, the main advantages of MSR are a result of the prerequisite that NG prevents the permeation of molten salts during normal operation. Once molten salt penetrates the NG, it leads to local hot spots that could easily attain temperatures of 1100–1200 °C at which the graphite damage rate is increased by a factor of two over the graphite damage rate at 700 °C [4].

In order to improve the inertness of NG toward molten salt, glassy carbon [5] or pyrolytic carbon [6] NG coatings have been utilized. On the other hand, with its low atomic number constituents, SiC has a series of advantages for use in reactors, such as good high

temperature properties, corrosion resistance, and low induced radioactivity after neutron irradiation, which is especially advantageous because it is environmentally benign. Furthermore, SiC has been successfully used in fusion reactors [7,8] and high temperature gas cooled reactors [9,10]. However, to our knowledge, the compatibility and the infiltration behavior between SiC and molten salt is scarcely studied and is therefore highly desirable. In our letter, the SiC coating is prepared on an NG substrate using chemical vapor deposition (CVD) to improve its infiltration resistance to liquid fluoride salt. The synchrotron radiation X-ray microbeam fluorescence (μ -XRF) results show that only a small amount of molten salt remains on or near the surface of the SiC coating after performing a static FLiNaK molten salt experiment at 5 atm. Our work offers a suitable candidate coating material for the development of MSR.

2. Experiment

The CVD was performed in a conventional tubular hot wall reactor, where Ar was used as protective gas during the heating and cooling process. The liquid precursor SiCl_4 was converted to the gas phase before entering the reactor through an evaporator bubbling hydrogen carrier gas. The NG substrate (IG-110, Toyo Tanso Co., Ltd.) was positioned at the isothermal zone, where the CVD was performed with the $\text{CH}_4/\text{SiCl}_4$ ratio of 0.25 in atmospheric pressure at 1150 °C. X-ray diffractometry (XRD, D8 Advance) was used to examine the crystalline structure of the SiC coating. Raman spectra were obtained using a SENTERRA Micro Raman spectrometer with a laser excitation at 633 nm. The morphology of the SiC coating was characterized by field-emission scanning electron

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microscopy (FE-SEM, LEO 1530VP). A eutectic composition was prepared using LiF (99.9% purity, from Aladdin Chemistry Co. Ltd.), NaF (99% purity, from Aladdin Chemistry Co. Ltd.), and KF (99% purity, from Acros Organics) salts mixed in proper proportions (46.5 mol% LiF/11.5 mol% NaF/42 mol% KF). The raw graphite sample, the graphite sample coated by SiC, and the molten salt were introduced in a high pressure reactor and heated at 650 °C for 12 h under 5 atm pressure. In order to avoid the impact of oxygen on the samples, all salt handling operations were performed inside a glove box with an inert argon atmosphere, and the high-pressure reactor was evacuated for 14 h using a molecular pump. The μ -XRF mappings were measured at the BL15U1 beamline station of the Shanghai Synchrotron Radiation Facility. The size of the incident beam and the energy of the X-ray in this study were approximately $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ and 20.05 keV, respectively. A Si/Li scintillation detector was used for data collection.

3. Results and discussion

The XRD spectra in Fig. 1a shows that the graphite phase of IG-110 NG is mainly hexagonal (graphite-2H: hexagonal, space group $P6_3/mmc\{P6_3/m2/m2/c\}$). Due to the wide and weak diffraction peaks, the SiC coating on IG-110 NG produced at

1150 °C exhibits only β -SiC phase with poor crystallinity. However, carbon peaks are also observed in the spectrum. The carbon peak originates from IG-110 NG substrate as an X-ray beam can penetrate through 7.8 μm -thick coating (see Fig. 2b). Fig. 1b shows the Raman spectra measured from the top surfaces of the IG-110 NG and the SiC coating. The occurrence of acoustic features, the absence of a second order band, and the appearance of broad longitudinal optical and transverse optical peaks indicate a heavily faulted β -SiC structure [11], which agrees with our XRD results. In order to test whether the SiC layer remains firm at high temperatures, a heat-cycle load experiment with a maximum holding temperature of 800 °C was conducted for the SiC coated sample. Even after 100 heat cycles, no scratches or cracks were observed with either an optical microscope or SEM, implying that the SiC coating has good compatibility with IG-110 NG at high temperatures. In addition, neutron irradiation will cause C atoms displacement, leading to crystallite dimensional change. The differential dimensional change by irradiation between SiC coating and NG is an issue to be studied in detail in future.

The surface of the SiC coating consists of multifaceted grains with diameters of $\sim 14\text{ }\mu\text{m}$, which interlock with each other to form a complex structure (Fig. 2a). Fig. 2b shows that a continuous and compact SiC layer ($\sim 7.8\text{ }\mu\text{m}$ in thickness) covers the surface of IG-110 NG, which has a number of micro pores with an average diameter of 3 μm [12]. After performing the static FLiNaK molten salt experiment for 12 h at 5 atm, the pores of the raw IG-110 NG are almost completely filled with salt particles, as shown in

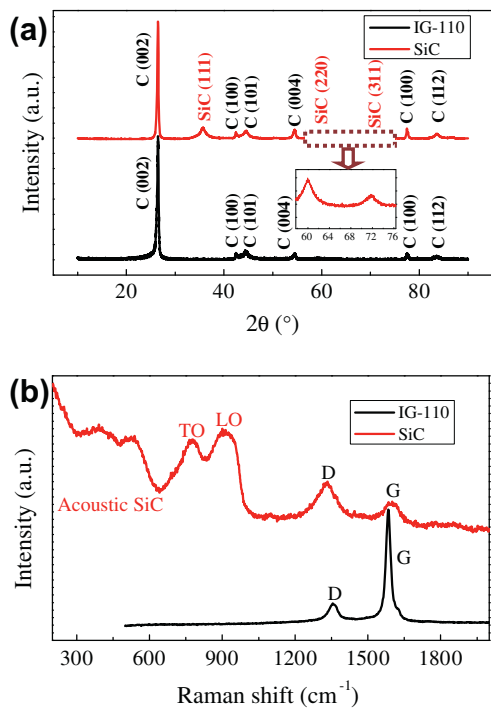


Fig. 1. (a) XRD patterns and (b) Raman spectra of the SiC coating and IG-110 NG.

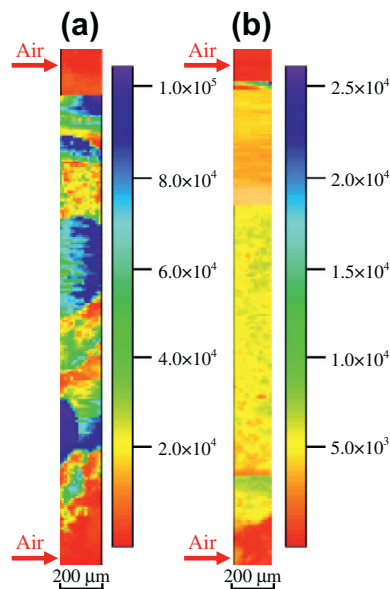


Fig. 3. μ -XRF element mapping of K from the cross-section in (a) IG-110 NG and (b) SiC coating corroded in FLiNaK molten salts at 650 °C for 12 h.

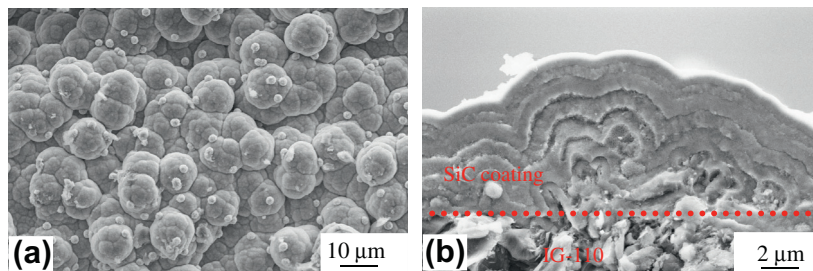


Fig. 2. SEM micrograph of the (a) surface morphology and (b) cross-section of the SiC coating.

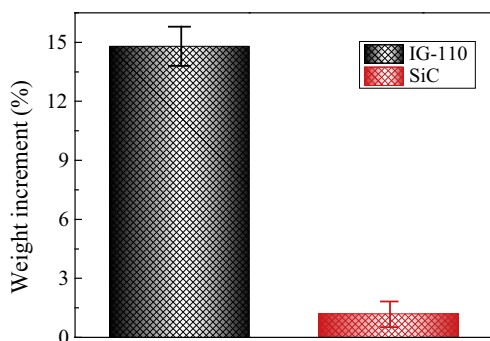


Fig. 4. Weight increment of raw and SiC-coated IG-110 NG impregnated by molten salt.

the μ -XRF element mapping of K of the cross-sectional sample (Fig. 3a). However, only a weak fluorescence count of K is observed on or near the surface of the SiC coating, as depicted in Fig. 3b. Clearly, the SiC coating can effectively protect IG-110 NG from liquid fluoride salt even at 5 atm. The weight increments of both samples were also compared to quantitatively investigate the infiltration of molten salt. From the results in Fig. 4, the weight increment of IG-110 NG decreases abruptly from 14.8% to 1.2% after being coated with SiC layer. Note that the crystallinity of β -SiC phase in the SiC coating deposited at 1150 °C is poor. Future studies will consider whether SiC coatings with higher crystallinity can more effectively protect NG from fluoride molten salt. Additionally, it is worth mentioning that chemical structure changes during the molten salt experiment, e.g., the formation of C–F bonds [13], are not considered because it has little effect on the infiltration of molten salt [6].

4. Conclusion

In conclusion, a continuous and compact SiC coating is prepared on an IG-110 NG substrate using CVD at 1150 °C. Under a test pressure of 5 atm, our results prove that the infiltration of molten salt into SiC coated NG is much less than that into uncoated NG. We believe this work demonstrates that SiC is a promising candidate material for the development of MSR.

Acknowledgements

This work is supported by the “Strategic Priority Research Program” of the Chinese Academy of Sciences (No. XDA02040200) and by the National Natural Science Foundation of China (Nos. 11075197, 91221101, 11375108, 11075097 and 11305240).

References

- [1] Technology roadmap for generation IV nuclear energy systems, in: Report USDOE/GIG-002-00, The U.S. DOE Nuclear research advisory committee and the generation IV international, Forum, 2002.
- [2] R.W. Moir, E. Teller, *Nucl. Technol.* 151 (2005) 334.
- [3] S. Delpech, C. Cabet, C. Slim, et al., *Mater. Today* 13 (2010) 34.
- [4] M.W. Rosenthal, P.N. Haubenreich, R.B. Briggs, The development status of molten-salt breeder reactors, Oak Ridge National Laboratory, ORNL-4812, 1972.
- [5] V. Bernardet, S. Gomes, S. Delpeux, et al., *J. Nucl. Mater.* 384 (2009) 292.
- [6] X. He, J. Song, L. Xu, et al., *J. Nucl. Mater.* 442 (2013) 306.
- [7] Y. Hirohata, T. Jinushi, Y. Yamauchi, et al., *Fusion Eng. Des.* 61 (2002) 699.
- [8] T. Hino, E. Hayashishita, Y. Yamauchi, et al., *Fusion Eng. Des.* 73 (2005) 51.
- [9] H. Nickel, H. Nabielek, G. Pott, et al., *Nucl. Eng. Des.* 217 (2002) 141.
- [10] G.K. Miller, D.A. Petti, D.J. Varacalle, et al., *J. Nucl. Mater.* 295 (2001) 205.
- [11] Y. Long, A. Javed, Z. Chen, et al., *Int. J. Appl. Ceram. Technol.* 10 (2013) 11.
- [12] T. Yamashina, T. Hino, *J. Nucl. Mater.* 162 (1989) 841.
- [13] X. Yang, S. Feng, X. Zhou, et al., *J. Phys. Chem. A* 116 (2012) 985.