

## MAX Phase Modified SiC Composites for Ceramic-Metal Hybrid Cladding Tubes

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### 1. Introduction

For application in LWRs with suppressed hydrogen release, a metal-ceramic as well as ceramic-metal hybrid cladding tube has been proposed [1-5]. A metal-ceramic hybrid cladding consists of an inner zirconium tube, and an outer SiC fiber-matrix SiC ceramic composite with surface coating as shown in Fig. 1 (left-hand side). The inner zirconium allows the matrix to remain fully sealed even if the ceramic matrix cracks through. The outer SiC composite can increase the safety margin by taking the merits of the SiC itself. In addition, the outermost layer prevents the dissolution of SiC during normal operation. On the other hand, a ceramic-metal hybrid cladding consists of an outer zirconium tube, and an inner SiC ceramic composite as shown in Fig. 1 (right-hand side). The outer zirconium protects the fuel rod from a corrosion during reactor operation, as in the present fuel claddings. The inner SiC composite, additionally, is designed to resist the severe oxidation under a postulated accident condition of a high-temperature steam environment.

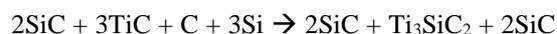
In the case of a ceramic-metal hybrid cladding tube, an inner SiC ceramic tube has been developed by forming a reaction-bonded SiC whose matrix was filled with MAX-phases. The MAX-phase is generated by the in-situ reaction of a pre-sintered body with Si-based melt. By forming the MAX phase in the SiC ceramic, the brittle nature with a low fracture toughness of a

conventional reaction-bonded SiC was modified. In this study, the formation of a  $Ti_3SiC_2$  MAX phase was investigated.

### 2. Methods and Results

A reaction bonding method is a method for obtaining a dense SiC sintered body by filling a SiC preformed structure with a molten Si. In this study, the process was modified to obtain the  $Ti_3SiC_2$  phase. One is a preform made of SiC and TiC powders, and the other is a Si melt that was alloyed with Ti. Three kinds of different compositions were investigated.

First, based on the following chemical reaction, SiC, TiC, and Si powders were prepared.



SiC in the starting materials remained as inert filler grains. The molar ratio of C/SiC was 0.5, and that of C/TiC was 0.33.

Second, a Ti foil/powder was placed on the SiC preform to be fused with Si melts at high temperature. The Ti-Si mixed melts infiltrated into the SiC preform.

Third, based on the following chemical reaction, TiC and Si powders were prepared.

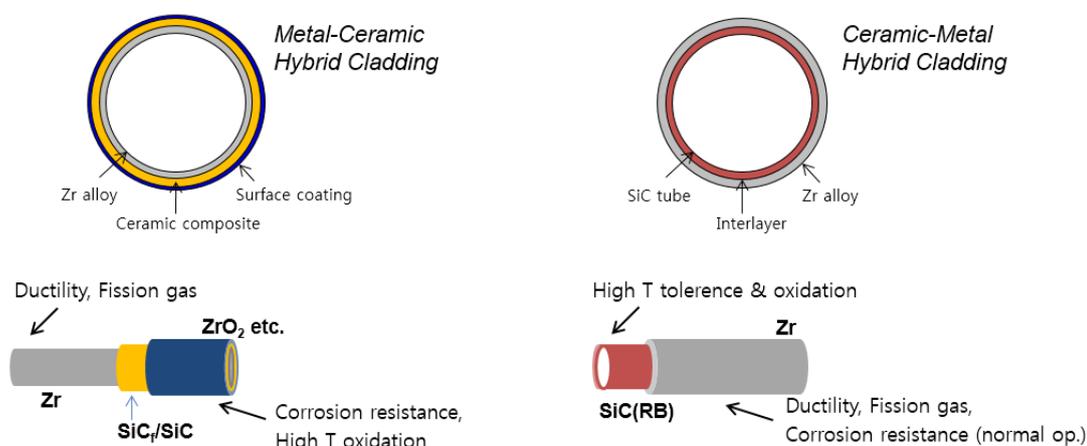
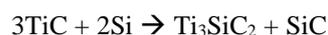


Fig. 1. Manufacturing process of the metal-ceramic hybrid fuel cladding tube. The first stage corresponds to the inner metal structure, and the second stage to the outer ceramic composite layer.

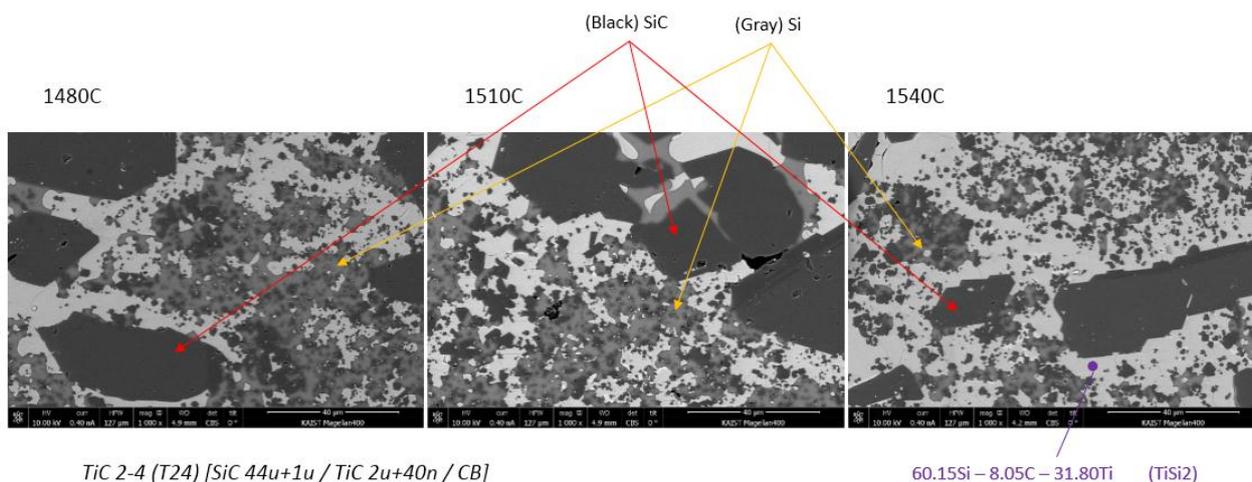


Fig. 2. Microstructures of reaction-bonded SiC using TiC-added SiC preforms which were sintered at 1480°C, 1510°C, and 1540°C for 2 h.

An inert filler of SiC was excluded, and the SiC could be formed only by the decomposition of TiC and reaction with Si.

#### Case 1. SiC + TiC (in starting composition)

Reaction-bonding was performed at 1480°C, 1510°C, and 1540°C for the TiC-contained SiC preforms, as shown in Fig. 2. As the temperature increased, the fraction of Si matrix (gray) was decreased while the fraction of TiSi<sub>2</sub> (white) was increased. The volume of SiC (black) was not changed, and Ti<sub>3</sub>SiC<sub>2</sub> was not observed in all samples. Table 1 summarizes the elemental analyses data for the phases having a gray contrast in Fig. 2.

Surplus Si melts are of help to densification, but willing to form Si-rich phase such as TiSi<sub>2</sub>. However, only the infiltration was insufficient when the mass of Si melt decreased.

Table 1. Results of elemental analyses

#	Si [at.%]	C [at.%]	Ti [at.%]	phase
1	62.37	35.13	2.49	SiC+TiSi <sub>2</sub>
2	59.87	8.37	31.67	TiSi <sub>2</sub>
3	62.42	9.95	27.65	TiSi <sub>2</sub>
4	60.15	8.05	31.80	TiSi <sub>2</sub>
5	60.03	8.05	31.47	TiSi <sub>2</sub>
6	60.90	10.35	28.74	TiSi <sub>2</sub>
7	58.89	10.23	30.88	TiSi <sub>2</sub>

#### Case 2. Si + Ti (in melt composition)

Ti foil and Ti powder were reacted with Si melts at above 1450°C. The chemical composition was varied depending on the position where Ti was placed initially, as shown in Fig. 3. However, the most profound phase other than Ti<sub>3</sub>SiC<sub>2</sub> was TiSi<sub>2</sub>. When the starting powders were controlled to have a molar ratio of Ti :

TiC : Si = 1 : 2: 1, the formation of Ti<sub>3</sub>SiC<sub>2</sub> was observed in the samples.

#### Case 3. TiC + Si (in reaction)

SiC was not used for the preparation of preforms. TiC and Si powders were mixed at a molar ratio of 3: 2. Since the low content of Si is undesirable to densification, the power compacts were pressurized during sintering. The pressure was varied from <1 MPa to 6 MPa. The formation of TiSi<sub>2</sub> along with large pores was notable when the samples were reaction-bonded without pressure. However, the MAX phase, i.e., Ti<sub>3</sub>SiC<sub>2</sub>, was obtained under pressurized sintering.

### 3. Conclusions

Reaction-bonded SiC was fabricated by modifying the matrix as the MAX phase. The formation of Ti<sub>3</sub>SiC<sub>2</sub> was investigated depending on the compositions of the preform and melt. In most cases, TiSi<sub>2</sub> was the preferential phase because of its lowest melting point in the Ti-Si-C system. The evidence of Ti<sub>3</sub>SiC<sub>2</sub> was the connection with the pressurizing.

#### Acknowledgment

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government(MSIP) (No. 2012M2A8A5000702)

#### REFERENCES

[1] Y.-I. Jung, B.-K. Choi, H.-G. Kim, D.-J. Park, J.-Y. Park, "Metal-ceramic hybrid fuel cladding tubes aiming at suppressed hydrogen release properties,"

Trans. Korean Nucl. Soc., 2012, May 17-18, Jeju, Korea.

[2] Y.-I. Jung, S.-H. Kim, J.-Y. Park, "Manufacturing process for the metal-ceramic hybrid fuel cladding tube," Trans. Korean Nucl. Soc., 2012, Oct. 25-26, Gyeongju, Korea.

[3] S.-H. Kim, Y.-I. Jung, D.-J. Park, H.-G. Kim, J.-Y. Park, S.-I. Hong, "Impregnation of the polycarbosilane preceramic polymer into SiC woven fabric," Trans. Korean Nucl. Soc., 2013, May 30-31, Gwangju, Korea.

[4] S.-H. Kim, Y.-I. Jung, D.-J. Park, J.-H. Park, H.-G. Kim, J.-Y. Park, S.-I. Hong, "Fabrication of SiCf/SiC composite by a polymer impregnation and pyrolysis process," Trans. Korean Nucl. Soc., 2013, Oct. 24-25, Gwangju, Korea.

[5] Y.-I. Jung, S.-H. Kim, D.-J. Park, J.-H. Park, J.-Y. Park, H.-G. Kim, Y.-H. Koo, "Three-point bending test for metal-ceramic hybrid fuel cladding tubes," Trans. Korean Nucl. Soc., 2014, May 29-30, Jeju, Korea.

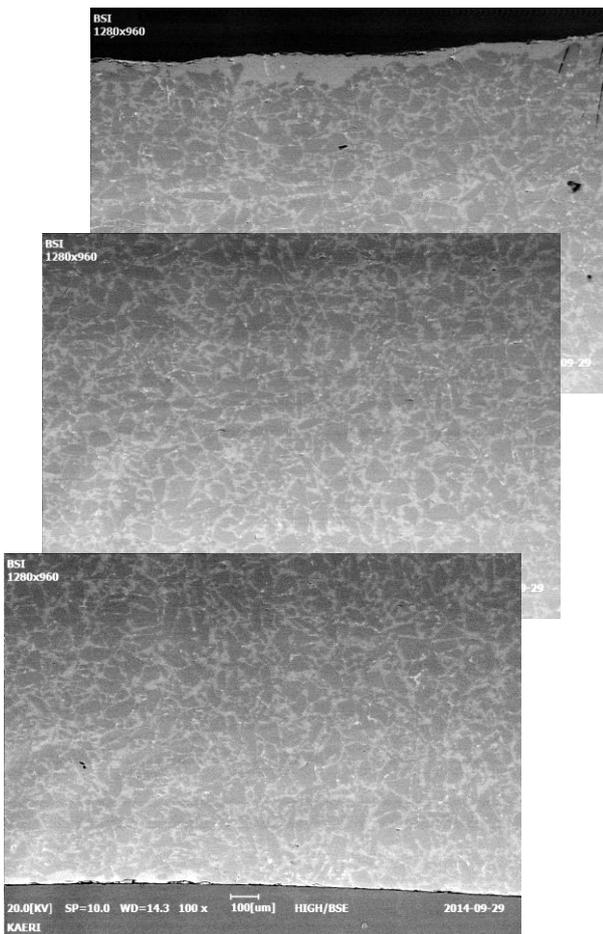


Fig. 3. Microstructures of reaction-bonded SiC using Ti foil placed on SiC preform. (1450°C, 4 h)