Transactions of the Korean Nuclear Society Spring Meeting
Gwangju, Korea, May 30-31, 2013

The Effect of SiC Coating by HPCS on the Oxidation of Zr alloy at High Temperature

Seonho Noh[a] , Kwangheon Park[a*,]
[a]Department of Nuclear Engineering, Kyung Hee University, Kyunggi-do, 446-701
[*]*Corresponding author: kpark@khu.ac.kr*

1. Introduction

In the field of nuclear plant safety analysis, various low probable accidental situations may result in fuel rod exposure. For that reason, ceramic coating on metal has been an interest in nuclear society. Silicon carbide (SiC) has been considered as a structural material for fusion reactor application because of its low afterheat, low residual activation and high temperature properties. Especially the SiC coating method by solution precess using polycarbosilane, which is C1 free preceramic polymer, is very useful method economically and environmentally. This study is to compare the oxidation behavior of Zr alloys and SiC coated Zr alloys.

2. Experimental

2.1 Specimen Preparation

The specimens used in this study are Zry-4 and Zirlo board. Table 1 shows the chemical composition of the specimen. Cladding tubes were cut to the height of 18mm~20mm. They were cleaned and etched

Table 1. Chemical composition of Zirconium alloys

	Zr (wt%)	Nb (wt%)	Sn (wt%)	Fe (wt%)	Cr (wt%)
Zry-4	bal.	-	1.35	0.2	0.1
Zirlo	bal.	1.0	1.0	0.1	-

2.2 Materials

Hydrido Polycarbosilane (HPCS) was supplied by Starfire System. co., and it's chemical structure is shown in figure. 1. The coating solution was prepared as 20wt% HPCS solution in toluene.

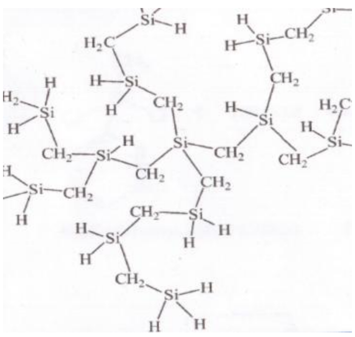

Figure 1. Chemical structure of Hydrido Polycarbosilane

2.3 Coating process

Etching → Dip coating → Drying → Curing → Pyrolysis

HPCS solution was coated on Zry-4, Zirlo with dip coating method. After dip coating, curing process was done at 150C in air. Pyrolysis was proceeded at 700C in nitrogen atmosphere to derive SiOC film.

The coating was done on half of the specimen to compare with metal layer and coated HPCS layer. The specimen appearance is shown in Figure 2.

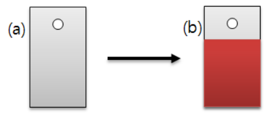

Figure 2. (a) before dip coating, (b) after dip coating

2.4 Experimental Procedures

The apparatus for the high-temperature steam testing of the coated Zirconium alloys used in this study is shown in Fig 3. In the tube furnace, there is an alumina tube in the center and the heater is surrounding the tube. In the case of steam experiment was established steam bubbler. Also an argon gas was supplied to the bubbler for steam generation. The furnace maintained at fixed temperatures i.e., 800C, 1000C, 1200C, and we put the specimens at the center of the tube. After a certain time passed, the specimens were pulled out. After the experiment the specimen was grounded and polished. The microstructures of the polished surface of the specimen were observed by an optical microscope.

Figure 3. Apparatus (tube furnace) for high temperature oxidation of coated Zr alloys in steam

3. Results

The specimens were observed in two parts, HPCS coated part and metal part by an optical microscope . Figure 4 shows the microstructure of Zr alloy part and HPCS coated part.

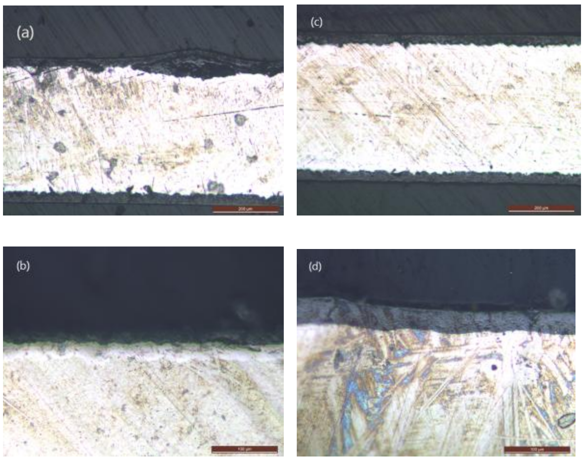

Figure 4. The microstructure of Zr alloys (a) oxide on the metal layer(1000C 15min), (b) oxide on metal layer(800C 60min), (c) oxide on HPCS layer(1000C 15min), (d) oxide on HPCS layer(800C 60min) in steam

Figure 4 shows that HPCS layer has been more oxidized than the metal layer.

When Zr alloys were oxidized at 1200C in steam, the metal layer looked normal, however, some portions in the HPCS layer looked abnormally grown. There were golden color compounds, i.e., zirconium nitride(ZrN) was found. Figure 5 shows the XRD patterns of the SiC.

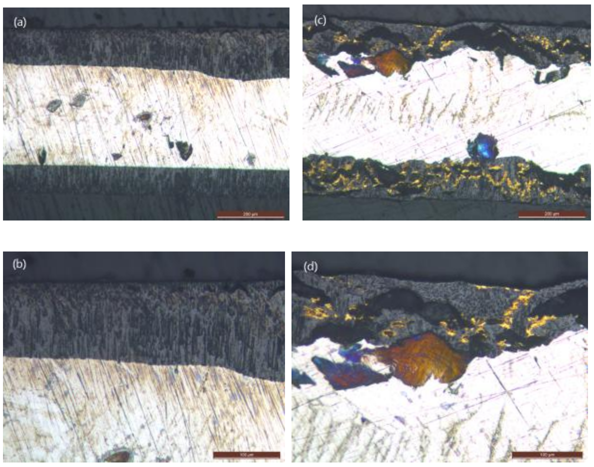

Figure 4. The microstructure of Zr alloys (a) oxide on the metal layer, (b) oxide on metal layer, (c) oxide on HPCS layer, (d) oxide on HPCS layer in steam at 1200C 10min

Reason for the creation of ZrN is that when pyrolysing the specimen in nitrogen atmosphere, nitrogen has been attached in the PCS coating. These nitrides seem to be the reason for the abnormal oxide growth; however, how nitrogen has not been found in the metal layer, how the nitride affected the oxide formation and why the metal layer did not have zirconium nitride need more experiments.

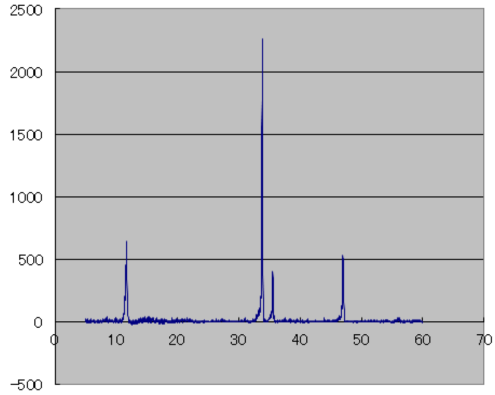

Figure 5. The XRD patterns of the Zr-alloys coated part

4. Conclusions

1200C HPCS layer contained abnormally grown oxide, golden spots were noticed, and they were zirconium nitride. When Zr alloys were Pyrolyzed in nitrogen atmosphere, Nitrogen had been attached to the HPCS layer, so the HPCS coated Zr alloys were oxidized more than normal Zr alloys in steam at high temperature around 800C~1200C. As ZrN is generated in this process, penetration is formed and oxidation is accelerated more abruptly. At 1000C and 800C the region of metal layer oxidized less than the HPCS region. When the Zr alloys were coated by the HPCS, little cracks had been made because of the tension. Therefore HPCS coated region had been oxidized more than the metal region.

REFERENCES

[1] Ly, H. Q., Taylor, R. J. and Heatley, F. Conversion of Polycarbosilane(PCS) to SiC-based ceramic part I, Characterization of PCS and Curing Product. *J. Mater. Sic.*, **36** (2001) 4037-4043.

[2] Li, Y. L., Fan, H., Su, D., Fasel, C. and Riedel, R. Synthesis, Structures and Properties of Bulk Si(O)C Ceramics from Polycarbosilane. *J. Am. Ceram. Soc.*, **92** (2009) 2175-2181

[3] Schiavon, M. A., Redondo, S.U.A., Pina, S. R. O. and Yoshida, I. V. P. Investigation on kinetics of thermal decomposition in polysiloxane networks used as precursors of silicon oxycarbide glasses. *J. Non-Cryst. Solids.*, **304** (2002) 922-100

[4] Lee, Y. J., Lee, J. H., Kim, S. R., Kwon, W. T., Oh, H., Klepeis, J. P., Teat, S. J. and Kim, Y. H. Synthesis and Characterization of Novel Preceramic Polymer for SiC. *J. Mater. Sci.*, **45** (2010) 1025-1031

[5] Kim, S.R., Kim, Y.H, Kim, J.I., Kim, J.I., Woo, C.H SiOC coating on STS316 by soft solution method with polyphenylcarbosilane, and its anti-corrosion properties. (2011)

[6] C. Duriez, T. dupont, B. Schmet, F. Enoch, Zircaloy-4 and M5 high temperature oxidation and nitriding in air, Journal of Nuclear Materials, vol. 380, p. 30-45(2008)