High Temperature Oxidation Behavior of Zirconium Silicides and Their Coating by Laser Cladding on the Zircaloy-4 Tube

Jae Joon Kim [a], Hyun Gil Kim [b], Ho Jin Ryu [a*]
[a]*Nuclear Fuel Materials laboratory, Department of Nuclear and Quantum Engineering, KAIST, Daehak-ro 291, Yuseong-gu, Daejeon,, 34141, Republic of Korea*
[b]*LWR Fuel Technology Division, KAERI, Daedeok-daero, 989-111, Yuseong-gu, Daejeon, 305-353, Republic of Korea*
[*]*Corresponding author: hojinryu@kaist.ac.kr*

1. Introduction

After Fukushima accident in 2011, the development of new cladding materials for light water reactors has been intensively investigated to prevent steam oxidation that causes the production of hydrogen and heat during Loss of Coolant Accident (LOCA). Various concepts have been proposed and several designs have been investigated. One of these ideas is the coating of the zirconium alloy cladding with a protective layer of oxidation-resistant materials, such as silicon carbide (SiC) [1], iron-chromium-aluminum (FeCrAl) alloy [2], and MAX phase materials [3]. A promising coating material for accident tolerant fuel cladding must have not only high temperature oxidation resistance, but also low neutron absorption, high adherence to the substrate, and thermal expansion similar to Zircaloy to prevent the interfacial stress caused by the thermal expansion difference between the coating and the substrate. Although existing attempts have an excellent performance in terms of high temperature oxidation resistance, several drawbacks have also been raised, such that SiC coating showed a yield strength limit at higher temperatures above 650 ℃, Fe in FeCrAl alloy coating can cause eutectic melting with substrate zirconium and showed unsatisfactory irradiation embrittlement, and MAX phase coating suffered difficulties in coating on the metal substrate.

The Zr-Si system has been proposed as one of promising protective coating materials for accident tolerant fuel cladding. During the oxidation of zirconium silicides, ZrO_2 is formed above the zirconium silicide since its lower formation Gibbs free energy compared to SiO_2. After this oxidation the zirconium concentration in zirconium silicides is reduced and the formation of SiO_2 is favored under the ZrO_2. This inner layer of SiO_2 serves as a barrier to oxygen and prevents further oxidation.

In this research, high-temperature oxidation behaviors of bulk zirconium silicides with different compositions were investigated. Coating of zirconium silicide on the surface of Zir-4 was performed using laser cladding method and its properties are also investigated.

2. Experimental and result

2.1 High temperature oxidation of bulk zirconium silicides.

Samples were prepared by vacuum arc-melting. Table 1 presents ratio of zirconium to silicon of samples.

Table. 1 Zr to Si ratio of samples

	Sample 1	*Sample 2*	*Sample3*
Zr to Si ratio	1:1	1:2	1:3

After fabrication of samples, heat treatment was applied at 1000 °C for 20 hours in order to give homogeneity to sample and they were cut to 5 mm × 5 mm × 1 mm size. Samples were washed using ultrasonic cleaning in ethanol for 5 min, and then dried. Oxidation experiments in 1200 °C steam and Ar mixture with 10 ml/min flow rate were carried out with a TGA. The temperature of the samples was increased with 50 °C/min and only Ar was supplied while raising the temperature. Microstructure and crystal structure were examined by scanning electron microscope (SEM) and X-ray diffraction (XRD) before and after oxidation.

Figure. 1~ 3 are showing microstructure of fabricated samples. The concentrations of the different brightness areas were investigated using energy dispersive x-ray spectroscopy (EDS) and are shown in the figures.

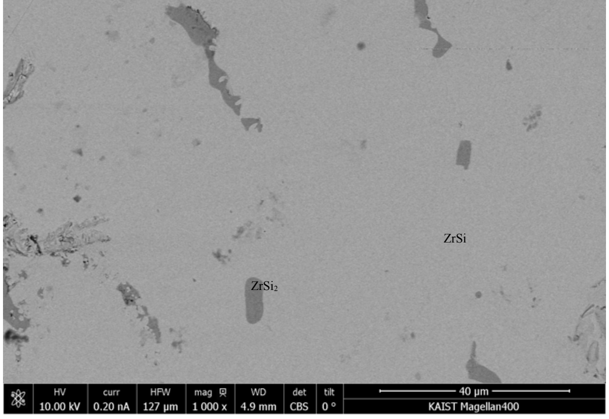


Figure 1. Microstructure of sample 1

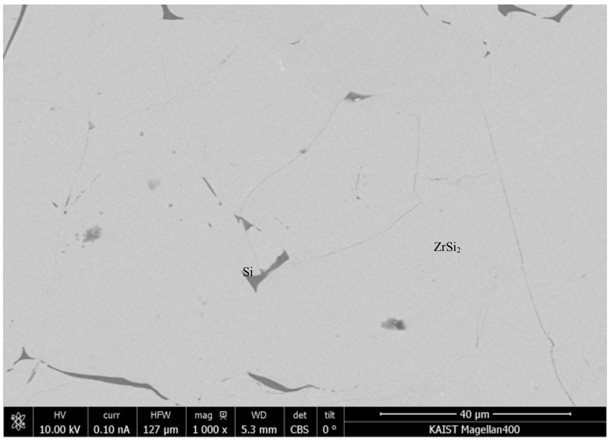


Figure 2. Microstructure of sample 2

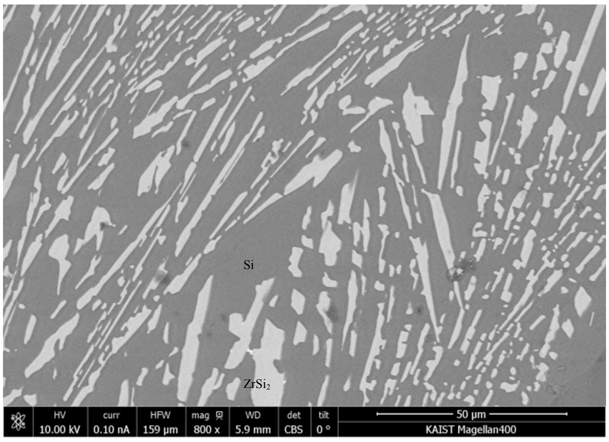


Figure 3. Microstructure of sample 3

Sample 1 consisted mainly of ZrSi and confirmed that a small amount of $ZrSi_2$ phase was observed. Sample 2 was predominantly $ZrSi_2$ and contained a small amount of pure silicon phase. In sample 3, $ZrSi_2$ and Si were uniformly mixed, but the volume ratio of Si was larger because the density of Si is smaller than that of $ZrSi_2$.

2.2 Coating of zirconium silicides on the Zir-4

The coating of zirconium silicides on the surface of the zircaloy-4 tube was performed by a laser-cladding method. The adhesion property of the coating was examined by a ring compression test. A photo of laser cladding equipment is shown in Figure 4. Applied laser power was 180 W and 0.3 mm hatching distance was used for coating. $ZrSi_2$ coating was best formed when the powder was mixed with Zr: Si = 1: 6 atomic ratios due to the difference in size between zirconium powder and silicon powder and existence of zirconium in substrate. Figure. 5 represents cross sectional image of zirconium silicides coating on the surface of Zir-4. $ZrSi_2$ was the main phase of the coating, and some pure Si and ZrSi were mixed.

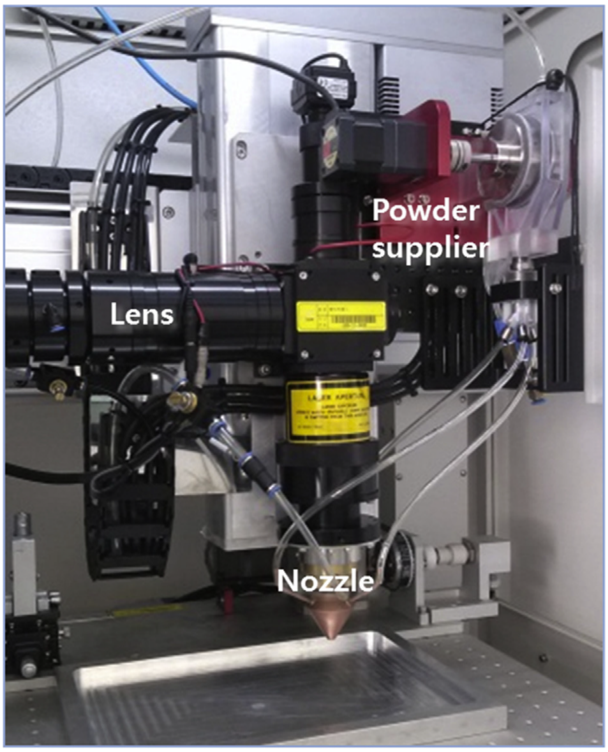
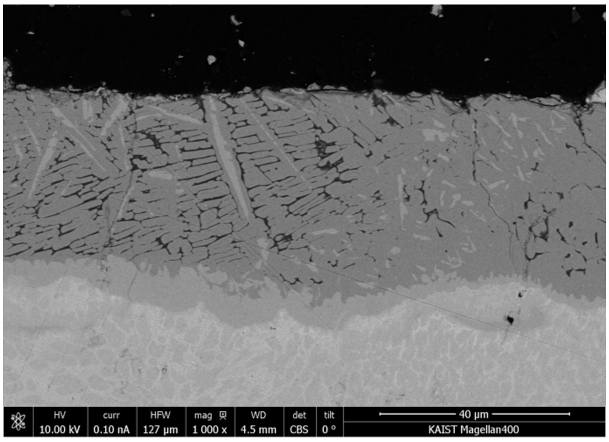


Figure. 4 Appearance of the laser cladding equipment [4]



Acknowledgments

This research was supported by the KUSTAR-KAIST Institute, KAIST, Korea.

REFERENCES

[1] C.P. Deck, G.M. Jacobsen, J. Sheeder, O. Gutierrez, J. Zhang, J. Stone, H.E. Khalifa, C.A. Back, Characterization of SiC-SiC composites for accident tolerant fuel cladding, J. Nucl. Mater. 466 (2015) 1–15. doi:10.1016/j.jnucmat.2015.08.020.

[2] Y. Dong, Y. Lu, J. Kong, J. Zhang, T. Li, Microstructure and mechanical properties of multi-component AlCrFeNiMo x high-entropy alloys, J. Alloys Compd. 573 (2013) 96–101. doi:10.1016/j.jallcom.2013.03.253.

[3] J.Y. He, W.H. Liu, H. Wang, Y. Wu, X.J. Liu, T.G. Nieh, Z.P. Lu, Effects of Al addition on structural evolution and tensile properties of the FeCoNiCrMn high-entropy alloy system, Acta Mater. 62 (2014) 105–113. doi:10.1016/j.actamat.2013.09.037.

[4] H.G. Kim, I.H. Kim, Y.I. Jung, D.J. Park, J.Y. Park, Y.H. Koo, Adhesion property and high-temperature oxidation behavior of Cr-coated Zircaloy-4 cladding tube prepared by 3D laser coating, Journal of Nuclear Materials, 465, (2015), 531-539