High Temperature Oxidation Behavior of the Aluminide Coated Refractory Samples in Steam Environment

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1. Introduction

Research has progressed actively to improve the safety of nuclear fuel, under the name of accident tolerant fuel (ATF), after Fukushima accident in 2011 [1]. Zirconium-based alloys have been used as cladding for commercial reactors for several decades because of their properties including desired physical properties, good thermal behavior, passive oxidation, low thermal neutron absorption cross-section and many more [2]. However, these alloys have a limiting behavior at high temperature accident situations. In other words, during accident situations, zirconium alloys show a relatively low strength. Furthermore, the high oxidation rate produces large amounts of hydrogen gas and increases brittleness. In addition, water injection as the accident is mitigated causing a thermal shock to take place rupturing the cladding and increases the safety concerns after the accident.

To mitigate these vulnerable cladding properties and behaviors at high temperatures, several candidates have been proposed such as SiC, FeCrAl, refractory metals, and coated materials. Among the candidates, refractory metals, such as molybdenum (Mo), have several merits including high strength in high temperature conditions and high melting point. In contrast, Mo shows a poor oxidation behavior as it does not form a passive protective layer during oxidation. Niobium (Nb) also shows reliable mechanical properties at high temperatures and has a high melting point, but has a poor oxidation resistance similar to Mo.

In this study, the oxidation resistance of molybdenum and niobium is enhanced by forming coating layers on the bare materials. Among several coating materials, aluminides (molybdenum aluminide and niobium aluminide) proved to be a good choice to improve the oxidation behavior. The aluminide-coated molybdenum and niobium are studied to verify the possibility to be used as cladding materials. The oxidation behavior of the coated samples has been analyzed using thermo-gravimetric analysis (TGA).

2. Method Choice and Experimental Procedure

2.1 Pack cementation

Pack cementation, a method that is based on solid-state diffusion, was chosen to be used as the coating method for the samples. Pack cementation is a simple reactive coating method that can be applied to complex geometries. Furthermore, the substrate and coating layer are chemically compatible due to the reactive nature of the coating. Pack cementation is one of the most common aluminide coating methods utilizing Al_2O_3, Al, and NaF powders.

The coating mechanism and the chemical equations of the aluminide coating with Al_2O_3, Al, NaF are described in Table I.

Table I: The reaction mechanism during pack cementation of aluminide coating [3]

Chemical equation
$NaF(g) + Al(s) \rightarrow AlF(g) + Na(g)$
$2NaF(g) + Al(s) \rightarrow AlF_2(g) + 2Na(g)$
$3NaF(g) + Al(s) \rightarrow AlF_3(g) + 3Na(g)$
$Mo / Nb + n\ Al \rightarrow Mo_3Al_8 / NbAl_3$
(n=8/3 for Mo, 3 for Nb)

2.2 Sample preparation

Disk-shape samples were fabricated from Mo, TZM (Mo-0.5Ti-0.1Zr-0.02C) as the substrates. Al_2O_3, Al, and NaF powders were prepared to coat the disk samples. The substrates were polished to remove contaminants and to get smooth surfaces.

After preparing the samples and the powders, the substrates were buried into the powder mixtures in a crucible. The ratio of the powder mixture of Al_2O_3, Al, and NaF is 50:30:20 wt%, respectively. The crucible was heated up to 950 ^oC in an argon environment. The coating took place and the coating layers were characterized using SEM, EDS, and XRD.

2.3 High temperature oxidation test

For the high temperature oxidation test, TGA was employed. Bare samples as well as the coated samples were used to perform the test on. The bare samples were tested as a reference for the sake of comparison. The TGA test was performed at 1200 ^oC in a steam atmosphere for 5 hours.

3. Results and Discussion

3.1 The microstructure of the coating layers

The microstructure and the XRD results of the aluminide-coated molybdenum sample are shown in Fig. 1 and Fig. 2, respectively. The sample was heat

treated at a temperature of 950 ºC for 3 hours. Mo_3Al_8 is observed in the molybdenum aluminide coating layer and the average thickness of the coating is 36 μm. The composition was determined using EDS and XRD. The results of the TZM sample match the results of the Mo sample almost perfectly with a slight difference in the coating thickness.

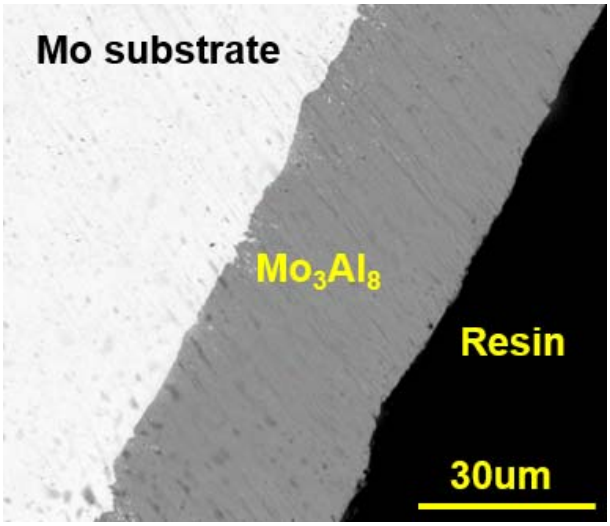

Fig. 1. The cross-section of the aluminide coated molybdenum sample

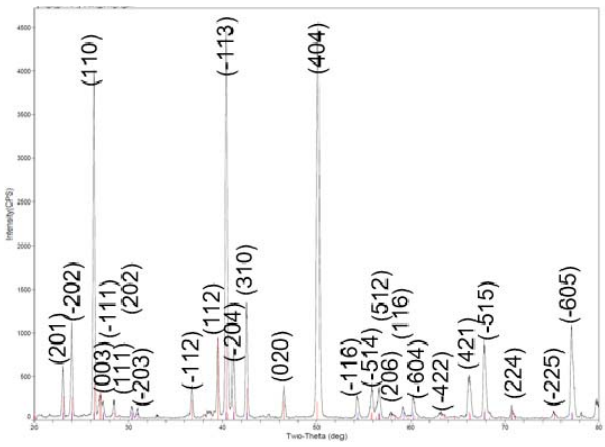

Fig. 2. The XRD result of the aluminide coated molybdenum sample

Fig. 3 and Fig. 4 describe the microstructure of the aluminide-coated niobium sample and the XRD result of the sample, respectively. Similar to the molybdenum aluminide sample, the coating was obtained after heat treatment at 950 ºC for 3 hours. The $NbAl_3$ coating layer, which has an average thickness of 33 μm, is observed.

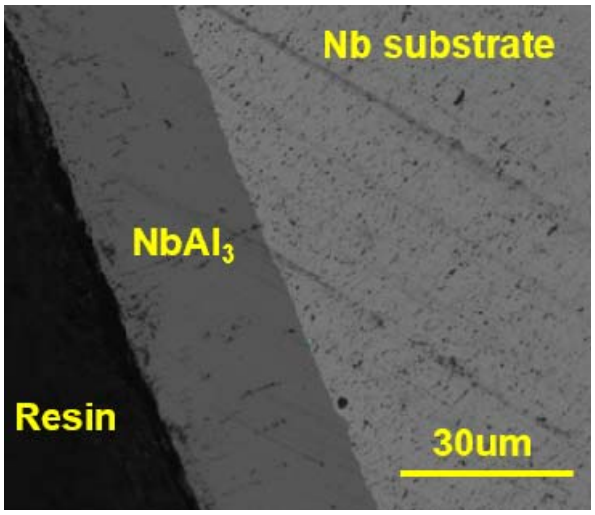

Fig. 3. The cross-section of the aluminide coated niobium sample

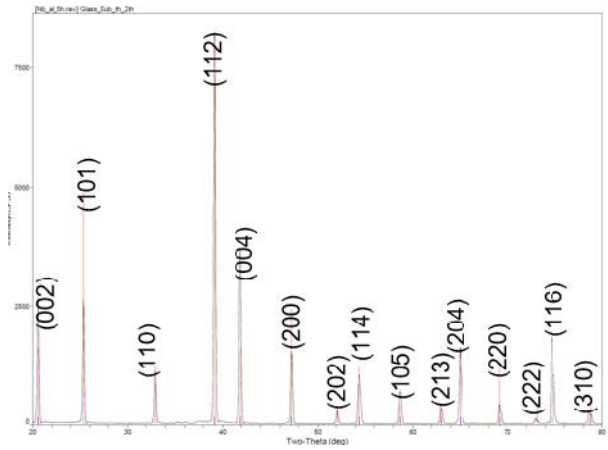

Fig. 4. The XRD result of the aluminide coated niobium sample

3.2 High temperature oxidation test

The coated samples were used for the high temperature oxidation tests. The samples were tested at 1200ºC in the TGA equipment in an atmosphere of argon and steam mixture. The samples were heated up at a rate of 50 ºC/min until the temperature reached 1200 ºC. The temperature was maintained at 1200 ºC for 2000 seconds. Fig. 5, Fig. 6, and Fig. 7 show the results of Mo, TZM, and Nb samples, respectively. Table II shows the final weight change of each sample.

The bare molybdenum shows a weight loss of 101 mg/cm^2 but coated molybdenum shows a weight gain of 4.4 mg/cm^2 as shown in Fig. 5. The bare sample loses the weight but the coated sample shows a slight weight gain indicating an oxidation resistant behavior. As molybdenum oxide is volatile at high temperatures, bare Mo samples show weight loss during oxidation.

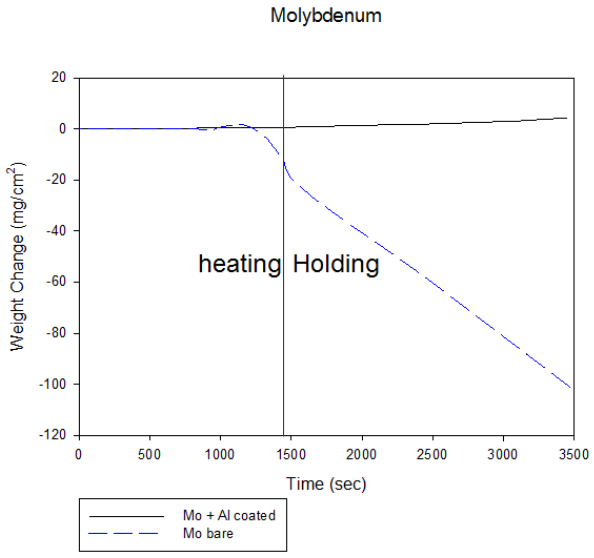

Fig. 5. The TGA test result of the molybdenum based sample

Fig. 6 shows the TGA test results of the TZM based samples. The bare TZM shows 90 mg/cm^2 weight loss but the coated TZM shows a weight gain of 4.2 mg/cm^2. The trend of the oxidation is very similar to that of molybdenum as TZM is a molybdenum-based alloy. The bare TZM shows relatively low weight loss when compared to bare Mo but the coated samples show similar weight gains.

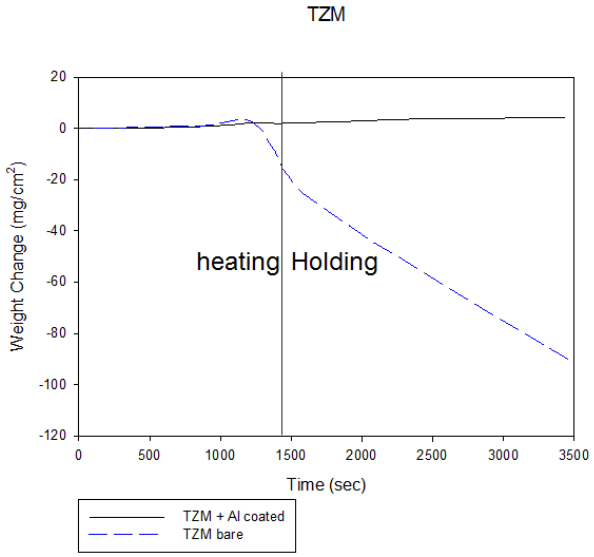

Fig. 6. The TGA test result of the TZM based sample

Fig. 7 is the TGA test result of the niobium-based samples. Unlike Mo, the bare niobium shows a weight gain of 20 mg/cm^2 and the coated niobium sample shows 3.2 mg/cm^2 weight gain. No weight loss was observed in the niobium-based samples because niobium oxide is not volatile at high temperatures.

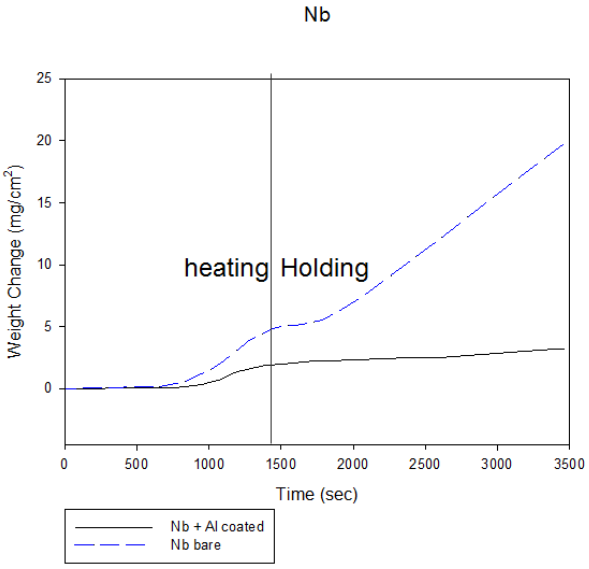

Fig. 7. The TGA test result of the niobium based sample

Table II: The summarized weight change of the TGA tests

Species		Weight change (mg/cm^2)
Mo	Bare	-101
	Coated	4.4
TZM	Bare	-90
	Coated	4.2
Nb	Bare	20
	Coated	3.2

4. Conclusions

In this study, Mo, TZM, and Nb were studied as candidates for ATF cladding. These materials have favorable properties in high temperature except the oxidation resistance. To improve the oxidation resistance of these materials, aluminide coating was conducted.

Aluminide coating was applied using the pack cementation method. After coating, the 36-μm Mo_3Al_8 coating layer was observed on the aluminide-coated molybdenum sample, which was coated at 950 °C for 3 hours. The 33-μm $NbAl_3$ coating layer was formed using the same conditions as the molybdenum coating.

The high temperature oxidation test in a steam atmosphere was conducted. The coated Mo, TZM, and Nb samples showed extremely lower weight change when compared to the bare samples. The niobium-based sample showed the lowest weight change among all the coated samples. The molybdenum and the TZM samples showed similar weight change results.

Acknowledgment

This study was supported by the KUSTAR-KAIST Institute, Republic of Korea.

REFERENCES

[1] S. J. Zinkle, K. a. Terrani, J. C. Gehin, L. J. Ott, and L. L. Snead, Accident tolerant fuels for LWRs: A perspective, J. Nucl. Mater., vol. 448, no. 1–3, pp. 374–379, 2014
[2] C. Lemaignan, 2.07 - Zirconium Alloys: Properties and Characteristics, Comprehensive Nuclear Materials, J. M. K. Editor-in-Chief: Rudy, Oxford, Elsevier: 217-232, 2012
[3] N. Kandasamy, L. L. Seigle, and F. J. Pennisi, The kinetics of gas transport in halide-activated aluminizing packs, Thin Solid Films, 84(1), 17-27, 1981.