

## Development of Silicide Coating on Molybdenum Alloy Cladding

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### 1. Introduction

Since the nuclear power plant accident in Fukushima, Japan in 2011, the importance of the accident-resistance fuel cladding has been widely recognized. The development of accident-resistant fuel cladding will contribute to the enhanced safety of nuclear power plants.

The accident tolerant fuel (ATF) concept is to delay the process following an accident by reducing the oxidation rate at high temperatures and to delay swelling and rupture of fuel claddings.

To develop the ATF cladding, alternative cladding materials cladding such as FeCrAl cladding, coated Zr and SiC cladding have been investigated. Currently, refractory alloys are also considered one of potential candidates for ATF cladding materials. Refractory elements such as molybdenum, niobium, and tantalum are considered as base elements for alternative cladding alloys [1]. Among the refractory elements, molybdenum has excellent mechanical properties at high temperatures and it has a low density of 6.25g/cm<sup>3</sup>, and a high melting point of 2030 °C. However the limitation of molybdenum cladding is considered active oxidation at elevated temperatures. Steam oxidation of molybdenum was conducted to provide assessment of its feasibility as cladding material, the oxidation rate at above 1000 °C, was slower than zirconium cladding alloys [2].

To mitigate the oxidation problem of molybdenum alloy cladding, potential designs for ATF refractory alloy cladding include multilayered designs with thin oxidation resistant layers on outer and inner surface of cladding.

In this paper, the protective silicide coating layer was deposited on refractory alloy material to enhance the oxidation resistance by pack cementation method. To see the enhancement, a thermos-gravimetric analysis method was conducted for both coated and bare samples.

### 2. Experiment

#### 2.1 Specimen preparation

In presented experiments, the reference substrates were selected as pure Mo and its alloy of TZM(Mo-0.5Ti-0.1Zr-0.02C), pure Nb in the form of disk cut to the size of 8Φ x 2 mm. These specimens were polished and cleaned before the coating deposition process. For the deposition process, pack cementation method was used. Pack cementation coating is a well-known method for a reactive coating that deposits one or more elements

on the surface of metallic structures. The coating layer grows by solid-state diffusion and leads to an excellent chemical compatibility with the substrate [3]. And pack cementation provides uniform coating layer deposition on the complex-shaped substrates.

For silicide coating by pack cementation, the substrate material is placed in a powder mixture. The powder mixture is commonly composed of a coating element (Si), an activator (NH<sub>4</sub>Cl) and a filler matrix (Al<sub>2</sub>O<sub>3</sub>). Then the container is placed in a tube furnace at 1200 °C with an argon flow atmosphere.

During pack cementation coating, the following chemical interactions occur on the surface of the molybdenum substrate as listed in Table 1. The activator material (NH<sub>4</sub>Cl) is decomposed into NH<sub>3</sub> and HCl. As the temperature increases, NH<sub>3</sub> is decomposed into N<sub>2</sub> and H<sub>2</sub> gasses. The decomposed HCl vapor reacts with Si powder in the mixture and forms volatile species SiCl<sub>4</sub>. SiCl<sub>4</sub> that interacts with Si powder in the powder mixture changes to volatile species such as SiCl<sub>3</sub>, SiCl<sub>2</sub> and SiCl. Chlorides such as SiH<sub>2</sub>Cl<sub>2</sub> and SiHCl<sub>3</sub> are formed from the reactions of hydrogen and chloride with Si powder. The combined HCl gas etches the surface of the substrate, and it enhances the diffusion of Si on the substrate surface region. Diffused Si reacts with Mo and results in the synthesis of a molybdenum silicide coating layer on the surface of the substrate. [3].

Table I: Chemical interactions during deposition process[4]

Chemical equation
$\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl}$
$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$
$4\text{HCl} + \text{Si} \rightarrow \text{SiCl}_4 + 4\text{H}$
$3\text{SiCl}_4 + \text{Si} \rightarrow 4\text{SiCl}_3$
$2\text{SiCl}_3 + \text{Si} \rightarrow 3\text{SiCl}_2$
$\text{SiCl}_2 + \text{Si} \rightarrow 2\text{SiCl}$
$\text{H} + \text{Cl} \rightarrow \text{HCl}$
$\text{Si} + \text{Cl}_2 + \text{H}_2 \rightarrow \text{SiH}_2\text{Cl}_2$
$\text{Si} + (3/2)\text{Cl}_2 + (1/2)\text{H}_2 \rightarrow \text{SiHCl}_3$
$\text{Mo} + 2\text{Si} \rightarrow \text{MoSi}_2$

After the pack cementation process, phase identification of coated specimens was carried out using X-ray diffraction (XRD). Microstructure and composition of the coating layer were determined using scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS), respectively.

#### 2.2 Oxidation tests

For the high temperature oxidation tests, the coated and the bare samples were washed using ultrasonic cleaning in alcohol for 20 min, and then dried. The dried samples were mounted in the equipment for high-temperature oxidation. Oxidation experiments of the coatings were conducted in air and steam atmosphere at high temperatures of 1000 °C (air) and 1200 °C (steam). For steam oxidation tests, a mixed gas of steam and Argon gas was induced at a 0.5 ml/min flow rate. The temperature of the samples was raised at 50 °C/min for both air and steam condition. [5]

### 3. Results

#### 3.1 Microstructure analysis

Fig. 1 shows the SEM image of silicide coating layer on molybdenum substrate. By the XRD pattern of the coating layer (Fig. 2), MoSi<sub>2</sub> layer was deposited on the substrate. Coating time was varied from 10 h to 20 h. Thickness was around 55 μm for 10 h.

Molybdenum silicide was also deposited well on TZM substrate. XRD pattern of the layer (Fig. 4) shows the same result with pure Mo. The thickness of the layer is less than pure Mo, there is inter-layer between outer molybdenum silicide and substrate. It was not detected by XRD but by the EDS, Mo<sub>5</sub>Si<sub>3</sub> was formed in the intermediate layer.

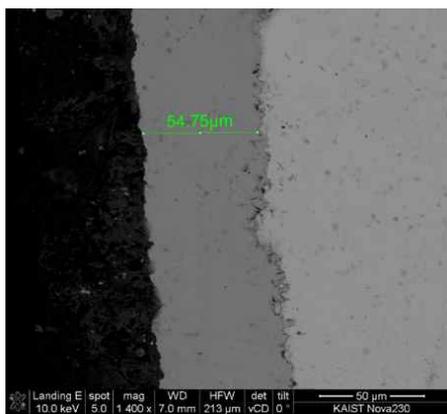


Fig. 1. SEM image (Mo substrate)

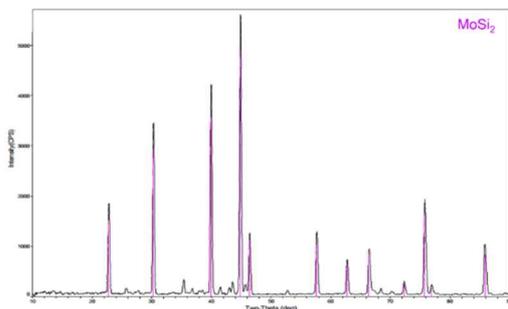


Fig. 2. XRD pattern of layer (Mo substrate)

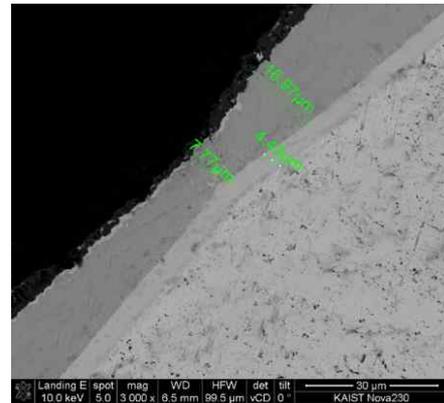


Fig. 3. SEM image (TZM substrate)

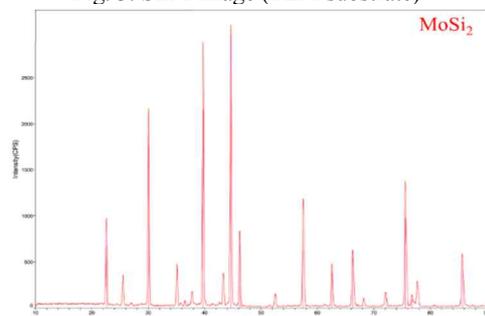


Fig. 4. XRD pattern of layer (TZM substrate)

Fig. 5 shows the SEM image of silicide coating layer on niobium substrate. By the XRD pattern of the coating layer (Fig. 6), NbSi<sub>2</sub> layer was deposited on the substrate. Thickness was around 7 μm for 10 h and also inter-layer was detected in SEM image. Intermediate layer composition was identified as Nb<sub>5</sub>Si<sub>3</sub> by the EDS results.

From the microstructure results above, both Mo and Nb substrate, silicide coating layer was successfully deposited.

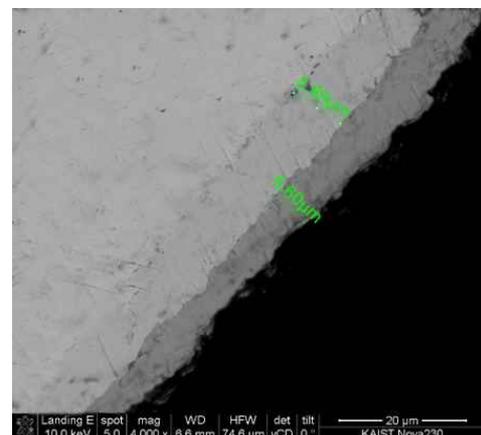


Fig. 5. SEM image (Nb substrate)

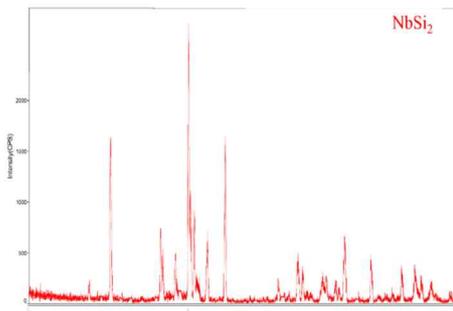


Fig. 6. XRD pattern of layer (Nb substrate)

### 3.2 Thermogravimetric analysis

Fig 7 shows the thermogravimetric analysis results for the various conditions. A,B, and C in the Fig. 7 represents the TG results in air condition. TG condition was conducted at 1000 °C for 2000 s. Air was induced at a 0.5ml/min flow rate. The temperature of the samples was raised at 50 °C/min rate. In the case of Mo substrate, mass change with the bare sample was 48.5%. With the protective silicide coating, the mass change was decreased down to 3.5%. Similar to the Mo substrate, the mass change was decreased from 85.3% to 5.1% in case of TZM substrate. Bare niobium sample has higher oxidation resistance result compare to Mo, TZM substrate. Mass change for the bare Nb sample was 11.7% and decreased to 7.7% for coated sample.

D,E, and F in the Fig. 7 represents the TG results in steam condition. TG condition was conducted at 1200 °C for 2000 s. Steam was induced at a 0.5ml/min flow rate. The temperature of the samples was raised at 50 °C/min rate. In the case of the Mo substrate, mass change with the bare sample was 60%. With the protective silicide coating, the mass change was decreased down to 10.6%. The mass change was decreased from 34.9% to 7% in case of TZM substrate. Mass change of the bare niobium sample was 23% and decreased to 2% for coated sample.

In both air and steam condition TG tests, the silicide coated sample shows much higher oxidation resistance result compare to the bare sample. The reason for these results is that the protective silicide layer forms a SiO<sub>2</sub> layer during the oxidation process. The outermost SiO<sub>2</sub> layer blocks the oxygen penetration to the substrate, it leads to reduce the oxidation of the substrate.

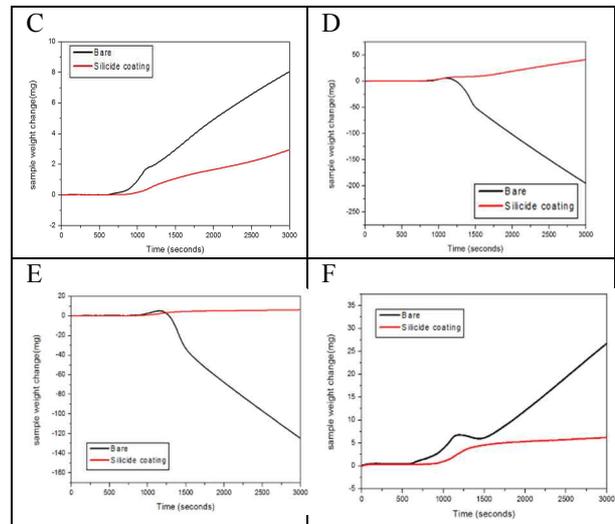
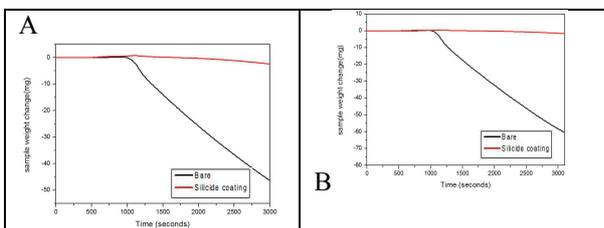


Fig. 7. TG test results (Air (A,B,C) / Steam (D,E,F))

## 4. Summary

The refractory alloy such as Mo and Nb are considered as one of the accident tolerant fuel (ATF) cladding materials due to its high temperature mechanical properties. However, those refractory alloys have a weak oxidation resistance at elevated temperatures. To modify the oxidation resistance of the refractory substrate, silicide coating on the cladding is considered. Molybdenum silicide (Niobium silicide) layers are oxidized to SiO<sub>2</sub> in an oxidation atmosphere. The SiO<sub>2</sub> protective layer isolates the substrate from the oxidizing atmosphere.

In this study, the pack cementation method was conducted to develop molybdenum silicide layers on molybdenum, TZM and niobium. It was found that the silicide layer was successfully deposited on the substrate from the microstructure analysis.

To measure the oxidation resistance, the thermogravimetric analysis was conducted for bare and silicide coated samples in air and steam condition. It was found that oxidation resistance was improved through the coating method from TG test results.

Further microstructure analysis for oxidized sample in the near future to analyze the oxidizing mechanism of the protective layer on the substrate.

## Acknowledgment

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