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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 enhaced 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. The current research for ATF can be categorized into three groups: First, modification of existing zirconium-based alloy cladding by improving the high temperature oxidation resistance and strength. Second, replacing Zirconium-based alloys with alternative metallic materials such as refractory elements with high temperature oxidation resistance and strength. Third, designing alternative fuel structures using ceramic and composite systems.

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 tantalium 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^3, and a high melting point of 2030℃. The limitation of molybdenum cladding is considered active oxidation at elevated temperatures. However, when the steam oxidation of molybdenum was conducted to provide assessment of its feasibility as cladding material, the oxidation rate at above 1000℃, 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 coating technique of silicide layers on molybdenum cladding, the coating mechanisms, and the oxidation behavior of the molybdenum silicide are summarized and preliminary results on silicide coating on molybdenum alloys are presented.

2. Review

2.1 Coating method

Several coating techniques are surveyed for cladding coating such as chemical vapor deposition (CVD), laser coating, and pack cementation coating. Among the coating techniques, pack cementation coating is a well-known method for 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]. Pack cementation provides homogeneous coating layer deposition on the complex geometries substrate.

For silicide coating by pack cementation, substrate material is placed in a powder mixture. The powder mixture is commonly composed of a coating element (Si), an activator (NH_4Cl) and a filler matrix (Al_2O_3). Then the container is placed in a furnace at a chosen temperature. The chemical activator in the powder mixture produces the transporting vapor materials during the deposition process. The chemical gradient between substrate and coating element in powder drives gas-phase diffusion generated within the container at a high temperature. Gaseous elements are easily driven to the substrate and surface reactions makes deposition on the substrate surface. Coating layer deposition is conducted at a temperature ranging from 1000℃ to 1200℃. The coating layer thickness is increased with the concentration of Si and the activator. However, above certain Si and activator composition, non-uniform growth of coating layer occurs. The coating layer thickness is enhanced with an increase in the holding time. Generally the coating layers form homogeneously more with a longer duration.

2.2 Mechanisms of deposition

During pack cementation coating, the following chemical interactions occur on the surface of the molybdenum substrate as listed in Table 1.

Table I: Chemical interactions during deposition process[4]

Chemical equation
$NH_4Cl \rightarrow NH_3 + HCl$
$2NH_3 \rightarrow N_2 + 3H_2$
$4HCl + Si \rightarrow SiCl_4 + 4H$
$3SiCl_4 + Si \rightarrow 4SiCl_3$
$2SiCl_3 + Si \rightarrow 3SiCl_2$
$SiCl_2 + Si \rightarrow 2SiCl$
$H + Cl \rightarrow HCl$
$Si+Cl_2+H_2 \rightarrow SiH_2Cl_2$

$$Si + (3/2)Cl_2 + (1/2)H_2 \rightarrow SiHCl_3$$
$$Mo + 2Si \rightarrow MoSi_2$$

During the process, activator material (NH_4Cl) is decomposed into NH_3 and HCl. As the temperature increases, NH_3 is decomposed into N_2 and H_2 gases. The decomposed HCl vapor reacts with Si powder in the mixture and forms volatile species $SiCl_4$. $SiCl_4$ that interacts with Si powder in the powder mixture, changes to volatile species such as $SiCl_3$, $SiCl_2$ and SiCl. Chlorides such as SiH_2Cl_2 and $SiHCl_3$ are formed from the reactions of hydrogen and chloride with Si powder. All the chlorides species reach the equilibrium partial pressure state at the processing temperature and therefore, are collectively responsible for the deposition of Si on the substrate. 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 surface of substrate. During the synthesis of Mo_3Si, Mo_5Si_3 phase coating layer is also deposited under the $MoSi_2$ coating layer [3].

2.3 Oxidation resistance of molybdenum silicide

Molybdenum silicide layers coated on a substrate as an oxidation resistance layer, are oxidized to MoO_3 and SiO_2 in an oxidation atmosphere. The ratio of $MoSi_2/Mo_5Si_3$ decreases after oxidation. It means that $MoSi_2$ coating layer decrease after oxidation and it follows the chemical reaction given below.

At a low temperature range (below 800℃), $MoSi_2$ is oxidized with following chemical interaction,

$$2MoSi_2 + 7O_2 \rightarrow 2MoO_3 + 4SiO_2$$

At a high temperature range (over 800℃), Oxidizing reaction occurs following chemical interaction,

$$5MoSi_2 + 7O_2 \rightarrow Mo_5O_3 + 7SiO_2$$
$$Mo_5O_3 + 10.5O_2 \rightarrow 5MoO_3 + 3SiO_2$$

After oxidizing reactions, the SiO_2 protective layer isolates the substrate from the oxidizing atmosphere. Molybdenum tri-oxide(MoO_3) accumulates below the SiO_2 layer, MoO_3 is a volatile material at a temperature above 800℃. The volume of formed SiO_2 is much greater than that of metal needed to form an oxide layer. Due to its high residual stress, cracks occur in vertical direction in the SiO_2 layer, so the volatile MoO_3 can escape through the cracks. Therefore at the beginning, the mass of coating decreases for a short time. After this period, SiO_2 layer heals by itself by forming new SiO_2 layer and the mass increases until the residual stress in the SiO_2 layer becomes high enough to form cracks again [5-7]

3. Experimental Results

2g (60wt%) of filler (Al_2O_3), 0.84 g (25wt%) of silicon powder and 0.5 g (15wt%) of activator (NH_4Cl) were mixed and placed in an alumina crucible. 8 mm x 10mm cylindrical molybdenum substrate (Nilaco Corporation) were positioned in the powder mixture. Then, the crucible was placed in a tube furnace, heating up to 1200℃ under an argon flowing condition. The heating rate was 10℃/min and the holding time was 4 hours. The microstructure of the layer was observed by scanning electron microscopy and the crystallographic information of layer was observed by X-ray diffraction analysis.

After the pack cementation process, Mo_3Si layer was deposited on the molybdenum substrate. It was confirmed by X-ray diffraction analyses as presented in Fig. 1. Molybdenum was also observed in X-ray diffraction because the Mo_3Si layer was non-homogeneous and as thin as less than 1 μm as as presented in Fig. 2.

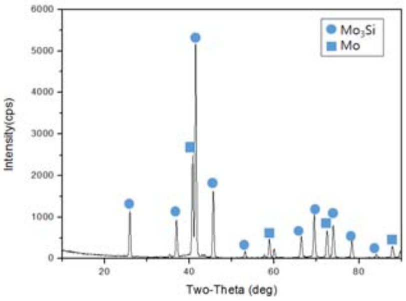

Fig. 1. XRD pattern of layer (1200℃, 4 hour)

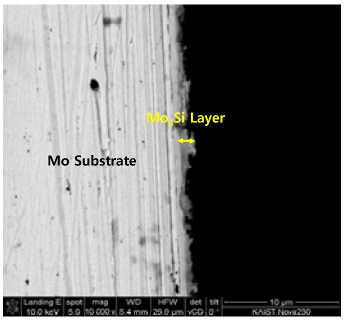

Fig. 2. SEM image (1200℃, 4 hour)

Instead of $MoSi_2$ or Mo_5Si_3 phase, Mo_3Si layer was deposited on the surface of the molybdenum substrate because the holding time was not enough to diffuse reactive elements in the powder mixture. In order to form $MoSi_2$ layer on the substrate, holding time is needed to be extend.

4. Summary

The molybdenum alloy is considered as one of the accident tolerant fuel (ATF) cladding materials due to its high temperature mechanical properties. However, molybdenum has a weak oxidation resistance at elevated temperatures. To modify the oxidation resistance of molybdenum cladding, silicide coating on the cladding is considered. Molybdenum silicide layers are oxidized to SiO_2 in an oxidation atmosphere. The SiO_2 protective layer isolates the substrate from the oxidizing atmosphere. Pack cementation deposition technique is widely adopted for silicide coating for molybdenum alloys due to its simple procedure, homogeneous coating quality and chemical compatibility.

In this study, the pack cementation method was conducted to develop molybdenum silicide layers on molybdenum alloys. It was found that the Mo_3Si layer was deposited on substrate instead of $MoSi_2$ because of short holding time. It means that through the extension of holding time, $MoSi_2$ layer can be formed on molybdenum substrate to enhance the oxidation resistance of molybdenum.

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