SURFACE ANALYSIS OF CESIUM MOLYBDATE DEPOSITED ON STAINLESS STEEL 316 IN SEVERE ACCIDENTS

HOANG XUAN THI, THI MAI DUNG DO[1,2], AND HISAYUKI SUEMATSU[1,2]

Center for Material Technology, Institute for Technology of Radioactive and Rare Elements, VINATOM: No. 48, Lang Ha Street, Dong Da District, Hanoi, Vietnam.

Department of Nuclear System Safety Engineering, Nagaoka University of Technology, Nagaoka, Japan.

E-mail: hoangthi.hus@gmail.com

[1] *Extreme Energy-Density Research Institute, Nagaoka University of Technology, Nagaoka, Japan.*

[2] *Department of Nuclear System Safety Engineering, Nagaoka University of Technology, Nagaoka, Japan.*

E-mail: suematsu@vos.nagaokaut.ac.jp, maidung@vos.nagaoaut.ac.jp

Abstract: The behavior of the Stainless Steel (SUS) after deposition of the Fission Product (FP) of Cesium in Severe Accidents (SA) is a major concern in developing understanding of nuclear material safety. The present research showed the interaction between the stainless steel surface and the FP of Cesium (Cs). The research was focus on SUS316 due to its important application as core internal and Cs_2MoO_4 due to its formation from Cs_2UO_4 under high temperature melting core in SA. The SUS316 samples were heated in the temperature range from 230^0C-960^0C in the argon gas with Cs_2MoO_4 vapor. The surfaces of SUS316 were analyzed by Optical microscope (**OM**), X-ray diffraction (**XRD**), Micro-RAMAN spectroscopy (**RAMAN**) and Scanning electron microscopy with energy dispersive X-rays spectroscopy (**SEM-EDS**). The results indicated that there are differences in without Cs_2MoO_4 and with Cs_2MoO_4 cases. There are formations of Chromium (Cr) oxide such as Cr_2O_3 and $FeCr_2O_4$ in without Cs_2MoO_4 case but in the case of with Cs_2MoO_4, only confirm the formation of Fe_3O_4 and there a transition from gamma (γ) to alpha (α) phase. We conclude that the SUS316 surface interacts complexly with Cs_2MoO_4 at high temperatures causing reactions and change in Cr content around SUS316 surface areas on causing phase transition from gamma γ to alpha α phase.

Keywords: *Severe accidents, SUS316, Cs_2MoO_4, deposition, high temperature, XRD, RAMAN, SEM-EDS.*

1. INTRODUCTION

On March 11, 2011, the Fukushima accident occurred after strong earthquake about 9 in richter scale. This earthquake created a 14 meter high tsunami that makes all diesel generators stopped functioning one hour after the off-site power supply was lost. This made the common-cause accident a long-duration-station blackout accident[1].

After the blackout, according to the conservative scenario, only 2 hours 20 min. for drop core water level to cause fuel rods heat up and start process of Zirconium alloy-oxidation. After 2 hours 30 min. the cladding starts melting and the vessel failures about 10 hours 30 min. later. The attack of the melt on the concrete basement melts through about 6 meters.

The temperature and fission products were not known around the core internal when accident happens, so some countries developed and used codes to predict temperature and fission products. In US, MELCOR and MAAP code was used. After 12 hours, the temperature increases to 1227^0C and pressure decreases below 1 MPa ≈ 10 atm. For the case

of fission product, there are two most important radioactive elements that have been studied. They are Cs and I. In Unit 2, CsI, Cs and Noble gas released after 80 hours and stable after 100 hours.

Cesium's behavior in the Reactor Coolant System (RCS) has to be defined also for planning the post-accident decommissioning. Cs has been considered to form CsOH and CsI. And a few studies have mentioned that Cs would rather form Cs_2MoO_4 than CsOH at high temp. In initial state, Cs exits in form of Cs_2UO_4, CsI, atomic Cs and CsO in some case. When the temperature increases around 1500K to 2300K, Cs_2UO_4 destructs to Cs_2MoO_4. And when the temperature reaches to 2500K, Cs_2MoO_4 vaporizes and deposits on the surface of material around core internal[2].

In boiling water reactors as well as pressure water reactors, there are three main groups of materials used to make all components in a light water reactor. They are stainless steel material, nickel base alloy and low alloy steel. In these 3 groups, stainless steel is most commonly used to make many components such as steam separator, core shroud, core support structure, jet pumps, control rods, CRD safe ends... In particular, the core internals around fuel rods are made by stainless steel due to its high durability with neutron radiation. Among the stainless steels, SUS304 and SUS316 are the most used. Recently SUS316 was used instead of SUS304 due to better IASCC resistance[3].

For all of these reasons, in this research, SUS316 and Cs_2MoO_4 were chosen as research objectives. Experiments carried out in this study will simulate high temperature conditions after Severe Accident in Argon gas environment. Cs_2MoO_4 compound was produced in form of vapor, diffused and then deposited on the surface of core internal that are usually made by SUS316. This research has 2 purposes that are research behavior of Cs_2MoO_4 in similar condition after accident and research degradation of SUS316 after Cs_2MoO_4's deposition.

2. EXPERIMENT

2.1. Research subjects and methodology

Research subjects in this research are Cesium Molybdate Cs_2MoO_4 and Stainless Steel SUS316. Cesium Molybdate Cs_2MoO_4 was crystalline powder that purchased from Sigma-Aldrich Company. The SUS316 samples were cut from SUS316 sheets. Their diameter is 15mm x 10mm x 1mm. After cutting, the SUS316 samples were polished by SiC paper, diamond powder and Al_2O_3 powders. And then the samples were cleaned with water and ethanol by AS38A ultrasonic cleaner. Subsequently the sample was heated at 200^0C for 24 hours to stabilize the surface. Finally, the sample was placed in a SiO_2 furnace to oxidation and deposition.

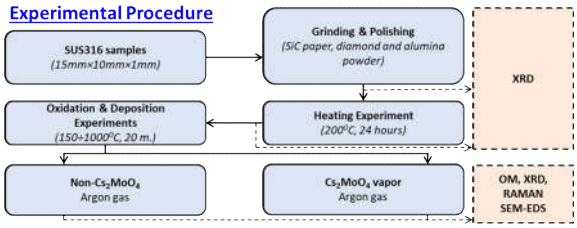

Fig. 1. Schedule of the research.

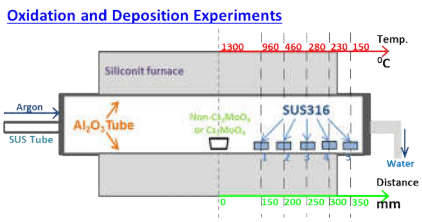

Fig. 2. Oxidation and Deposition experiments.

Oxidation and deposition experiments were conducted in 150-960^0C range. The keep time is 20 minute and the Argon gas is 0.1 L/min. The temperature at the center of furnace is 1300^0C. There are 5 SUS316 samples in each experiment, the temperature of each SUS316 samples are 150-230-260-460 and 960^0C. After holding the temperature for 20 minutes, the furnace was turned off and the SUS316 samples were cooled in argon gas flow (0.1L/min.) to room temperature.

The SUS316 samples that obtained after oxidation and deposit experiment will be analyzed surface by some methods that are Optical microscope (**OM**), X-ray diffraction (**XRD**), Micro-RAMAN spectroscopy (**RAMAN**) and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (**SEM-EDS**).

2.2. Results & Discussions

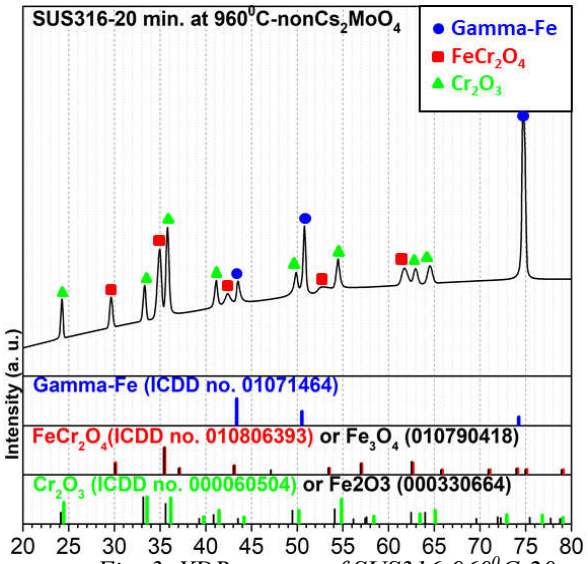

Fig. 3. XDR pattern of SUS316-960^{0}C-20 min.-nonCs_2MoO_4

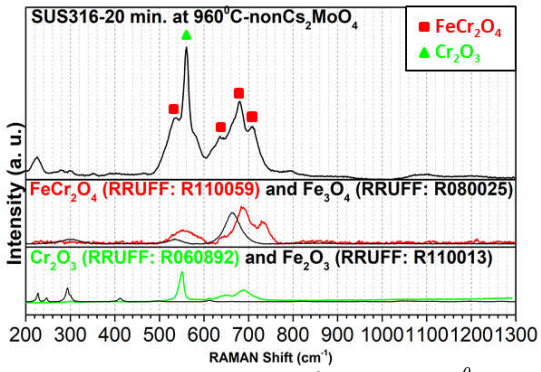

Fig. 4. RAMAN spectrum of SUS316-960^{0}C-20 min.-nonCs_2MoO_4

Peak	Atom %
Cr-K	93.35
Fe-K	6.65
Total	100

Table 1. SEM-EDS analysis of SUS316-960^{0}C-20 min.-nonCs_2MoO_4

Fig. 3, Fig. 4 and Table 1 show the results of 960^{0}C SUS316 sample after oxidation experiment with non-Cs_2MoO_4. The XRD results show the formation of the two oxides on the sample surface. They are Fe_2O_3 and Fe_3O_4. However, the XRD patterns of Fe_2O_3 and Cr_2O_3 are the same, similar case of Fe_3O_4 and $FeCr_2O_4$. The results of RAMAN confirm the formation of $FeCr_2O_4$ and Cr_2O_3. Finally SEM-EDS method was used to determine the ratio between Cr and Fe on the sample surface. The SEM-EDS results show that the Cr content ratio was 93.35%. It means that Cr_2O_3 and $FeCr_2O_4$ were formed on the surface of 960^{0}C SUS316 sample and Cr_2O_3 was formed in large amounts**.**

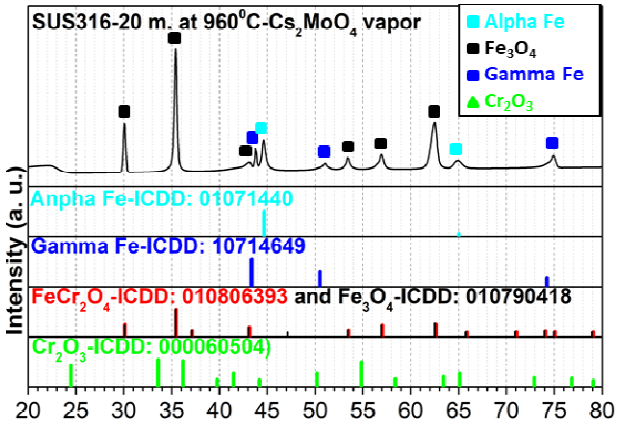

Fig. 5. XDR pattern of SUS316-960^{0}C-20 min.-nonCs_2MoO_4

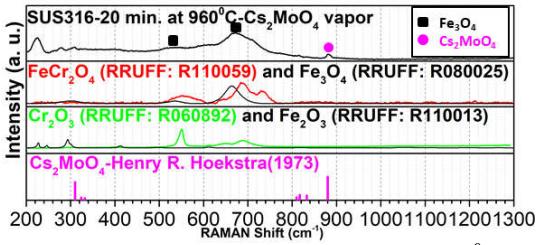

Fig. 6. RAMAN spectrum of SUS316-960^{0}C-20 min.-nonCs_2MoO_4

Peaks	Atom%
Cr K	2.32
Fe K	94.54
Cs L	3.14
Total	100

Table 2. SEM-EDS analysis of SUS316-960^{0}C-20 min.-nonCs_2MoO_4

Results of XRD, RAMAN analysis in the case of with-Cs_2MoO_4 are showed in Fig. 5-6. These results showed that α-phase, $FeCr_2O_4$/Fe_3O_4 was formed on the surface of 960^{0}C SUS316 sample and there was no appearance of any Chromium Oxide Cr_2O_3 as was known in the case of without-Cs_2MoO_4 case. That means there was a gas-solid phase reaction between Cs_2MoO_4 vapor and Cr_2O_3 on the surface of SUS316 at high temperature. This reaction may

have caused a decrease in chromium content around SUS316 surface areas on causing phase transition from gamma γ to alpha α phase.

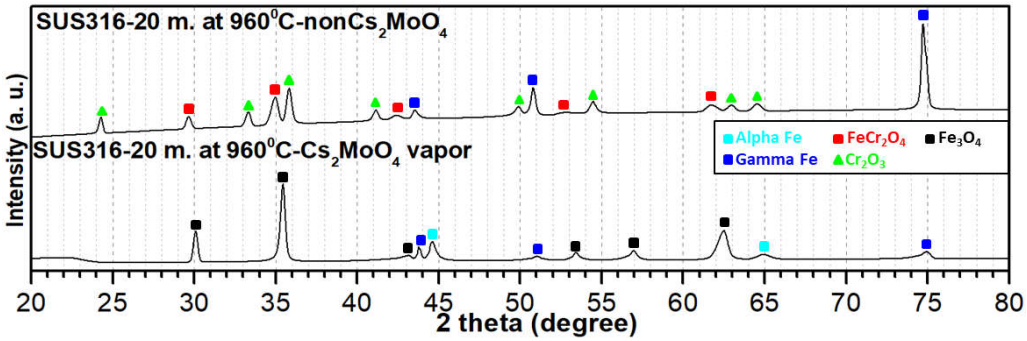

Fig.7. XDR pattern of SUS316-960^{0}C-20 min.-nonCs_2MoO_4

The XRD results of 460^{0}C-280^{0}C-230^{0}C samples with non-Cs_2MoO_4 are showed in Fig. 8. The XRD analysis points that only observe the gamma phase on the surface of 460^{0}C-280^{0}C-230^{0}C samples. The RAMAN results of 460^{0}C-280^{0}C-230^{0}C samples with non-Cs_2MoO_4 are showed in Fig. 9. There are very small amounts of Fe_2O_3 and Fe_3O_4 on the surface of 460^{0}C sample.

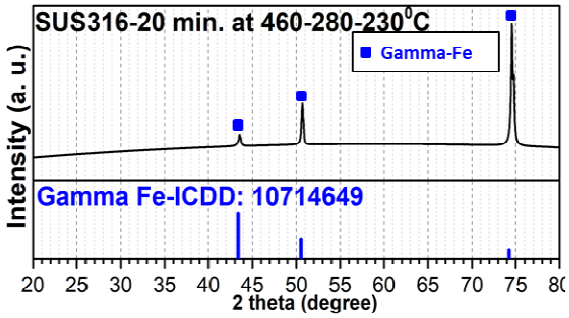

Fig. 8. XDR pattern of SUS316-460^{0}C-280^{0}C-230^{0}C-20 min.- Cs_2MoO_4

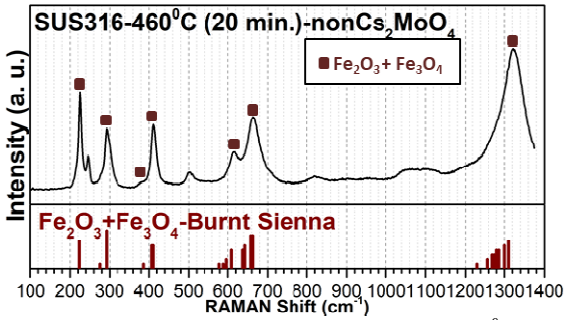

Fig. 9. RAMAN spectrum of SUS316-460^{0}C-280^{0}C-230^{0}C-20 min.- Cs_2MoO_4

3. CONCLUSION

For the case of condition that is 20 min. keep time, 0.1 L/min. Argon gas and non-Cs_2MoO_4: Confirm the form of Cr_2O_3 and $FeCr_2O_4$ on the surface of 960^{0}C SUS316 sample by XRD, RAMAN and SEM-EDS analysis. And confirm the form of the mixture of Fe_2O_3 and Fe_3O_4 on the surface of 460^{0}C SUS316 by RAMAN analysis. For the case of condition that is 20 min. keep time, 0.1 L/min. Argon gas and Cs_2MoO_4: Confirm the form of α-phase and $FeCr_2O_4$/Fe_3O_4 on the surface of 960^{0}C SUS316 sample by XRD analysis. After 5 days drying the samples in closed box that has silica gel, the XRD analysis results of 960^{0}C, 280^{0}C, 230^{0}C and 150^{0}C samples show the appearance of new peaks around 25^0 and 35^0 (2-theta).

4. REFERENCES

[1] Bal Raj Sehgal, et al. Light water reactor safety: A Historical Reaview.

[2] Dubourg, R., Faure-Geors, H., Nicaise, G., & Barrachin, M. (2005).

[3] R. W. Staehle, "Anatomy of Proactivity," presented at the Proceedings of the Internationla Symposium on Research for Agìn Management of LWR and Its Future Trend (The 15th Aniversary of INSS), October 22-23, 2007, Fukui, Japan, Eds. B. L. Eyre and I. Kimura, 2008, pp. 29-115.

PHÂN TÍCH BỀ MẶT CỦA THÉP KHÔNG GỈ 316 NHƯNG TỤ XÊSI MOLYBDATE TRONG TAI NẠN NGHIÊM TRỌNG

HOANG XUAN THI, THI MAI DUNG DO[1,2], AND HISAYUKI SUEMATSU[1,2]

Center for Material Technology, Institute for Technology of Radioactive and Rare Elements, VINATOM: No. 48, Lang Ha Street, Dong Da District, Hanoi, Vietnam.

Department of Nuclear System Safety Engineering, Nagaoka University of Technology, Nagaoka, Japan.

E-mail: hoangthi.hus@gmail.com

[1] *Extreme Energy-Density Research Institute, Nagaoka University of Technology, Nagaoka, Japan.*

[2] *Department of Nuclear System Safety Engineering, Nagaoka University of Technology, Nagaoka, Japan.*

E-mail: suematsu@vos.nagaokaut.ac.jp, maidung@vos.nagaoaut.ac.jp

Tóm tắt: Hành vi của thép không gỉ (SUS) sau khi ngưng tụ sản phẩm phân hạch (FP) của Caesium trong tai nạn nghiêm trọng (SA) là mối quan tâm chính trong việc phát triển sự hiểu biết về an toàn vật liệu hạt nhân. Nghiên cứu hiện tại cho thấy sự tương tác giữa bề mặt thép không gỉ và sản phẩm phân hạch (FP) của Caesium (Cs). Nghiên cứu tập trung vào thép không gỉ SUS316 do ứng dụng quan trọng của nó làm chi tiết lõi lò và hợp chất Cs_2MoO_4 được tạo thành từ Cs_2UO_4 trong điều kiện nhiệt độ cao trong các tai nạn nghiêm trọng (SA). Các mẫu thép không gỉ SUS316 được gia nhiệt trong khoảng nhiệt độ từ 230^0C đến 960^0C trong môi trường khí argon có hơi Cs_2MoO_4. Bề mặt của SUS316 được phân tích bằng kính hiển vi quang học (OM), nhiễu xạ tia X (XRD), quang phổ Micro-RAMAN (RAMAN) và kính hiển vi điện tử quét với quang phổ tia X tán sắc năng lượng (SEM-EDS). Kết quả chỉ ra rằng có sự khác biệt khi không có Cs_2MoO_4 và với các trường hợp có mặt Cs_2MoO_4. Oxit Crôm (Cr) Cr_2O_3 và $FeCr_2O_4$ được tìm thấy trong trường hợp không-Cs_2MoO_4, nhưng trong trường hợp có-Cs_2MoO_4, chỉ xác nhận sự hình thành Fe_3O_4 và sự có mặt của pha anpha (α). Chúng tôi kết luận rằng bề mặt SUS316 đã tương tác phức tạp với Cs_2MoO_4 ở nhiệt độ cao gây ra phản ứng và thay đổi hàm lượng Cr tại vùng bề mặt SUS316 dẫn đến sự chuyển pha từ gamma γ sang pha alpha α.
Từ khóa: *Tai nạn nghiêm trọng, SUS316, Cs_2MoO_4, lắng đọng, nhiệt độ cao, OM, XRD, RAMAN, SEM-EDS.*