

# Analysis of a metallic precipitates in an irradiated simulated fuel

Y. H. Jung, B. O. Yoo, S. B. Ahn, U.S. Rhu

Korea Atomic Energy Research Institute

150, Dukjin-Dong, Yuseong-gu, Daejeon, 305-353, Korea

E-mail : [nyhjung@kaeri.re.kr](mailto:nyhjung@kaeri.re.kr), Telephone: 82-42-868-8459, FAX : 82-42-868-8420

## Abstract

A simulated fuel specimen which was irradiated at the HANARO research reactor up to 3,300 MWd/tU of a burn-up at the condition of 36 kW/m of a maximum linear power was studied by a shielded EPMA (Electron Probe Micro-Analyzer). This study concentrated on the metallic precipitates of the irradiated simulated fuel specimen which contained lots of fission products. Among the several properties of the metallic precipitate, its size and composition were investigated. A large metallic inclusion was also observed in the irradiated simulated fuel, from which X-ray photographs were taken to analyze its properties.

**Keywords:** simulated fuel, HANARO, fission product, metallic precipitate, large metallic inclusion.

## 1. Introduction

Previous studies by adopting a post-irradiation test have been performed for an irradiated DUPIC(Direct Use of Spent PWR Fuel in CANDU Reactors) fuel, which was fabricated from spent fuel with an oxidation and a reduction process[1-3]. Because a fission product affects the electric and thermal conductivities of a fuel, a large quantity of it changes the fuel performance of a fuel especially for high burn-up fuels, therefore, characterizing a metallic precipitate through a post irradiation examination is important. Molybdenum is the least noble element in such alloys and it is known that this type of precipitate has a hexagonal structure and its homogeneity is usually maintained. It is also widely known that the density of this precipitate in a fuel at a high temperature increases at around  $r/r_0=0.6$ , which results from a movement of Mo and Ru to a lower temperature region due to an oxidation. The oxygen potential of a dioxide,  $\text{MoO}_2$ , in an equilibrium state with in alloys, is comparable to the oxygen potential of a fuel within its homogeneity region [4].

## 2. Experimental preparations

EPMA (Electron Probe Micro Analyzer, SX-50R, CAMECA, FRANCE) was used to identify the major constituents of the metallic precipitates in this study. The specimen holder as a part of the equipment was shielded from a radiation leakage and WDS (Wavelength Dispersive

Spectroscopy) count windows containing lead and tungsten were used to permit an analysis of the irradiated nuclear fuel. The maximum allowed radiation activity in this EPMA was up to  $3.7 \times 10^{10}$  Bq.

### 2.1. Preparation of the irradiated simulated fuel

A specimen of irradiated simulated fuel was irradiated at the HANARO research reactor up to 3,300 MWd/tU of a burn-up with 36 kW/m of a maximum linear power and 32 kW/m of an average linear power. The post irradiation examination was performed in the IMEF (Irradiated Materials Examination Facility) hot cell in KAERI.

Irradiation rig to retain the irradiated simulated fuel was fabricated with Al-6061 and its dimensions were 960 mm in length, 56 mm in diameter and 3.0 kg in weight. Cladding tube was fabricated with Zircaloy-4 with the dimensions of 0.66 mm of a thickness, 10.08 mm of an inner diameter and 199 mm on length. Dimensions of the sintered pellet were 10 mm in length and 10.6 mm in diameter with a theoretical density of 10.07.

After an irradiation in HANARO, the specimen for observing the microstructure was taken at a 5 mm thickness with a diamond wheel at a position of 100 mm from the top of the cladding tube.

## 3. Results and discussion

### 3.1. Discussion on the metallic precipitates

Fig. 1 depicts the distribution of the metallic precipitate in the radial direction. From the center of the specimen, 10 parts with the same distance of 400  $\mu\text{m}$  are selected arbitrarily and 200 SEM magnifications are taken. Among the several metallic precipitates, the average size was obtained from 5 different images. The metallic precipitates observed in the fresh simulated fuel were  $0.5 \sim 1.0 \mu\text{m}$ , while those of the irradiated simulated fuel were  $2 \sim 3.5 \mu\text{m}$  in diameter. It is believed that the initially produced precipitates during the sintering were grown by coalescence with newly produced fission products during an irradiation. Also it was found that the size of the metallic precipitate became smaller from the center to the surface of a specimen.

Fig. 1 (b) shows the quantitative results for the Mo element at 50 points in the radial direction. It is well known that Mo also exists as an oxide form in a fuel matrix. Because a metallic precipitate is distributed abnormally in a fuel, the analysis of Mo was performed with EPMA at the grain boundary rather than the size of a grain. Among the several EPMA methods, the TV mode was chosen with a magnification of 10,000 times. Although the concentration of Mo may increase in a metallic precipitate, the trend of Mo can be estimated if an analysis is performed at an arbitrary point with the same distance in the radial direction. In Fig. 1(b), the concentration profile of the molybdenum dissolved in the fuel matrix, trend represents that the concentration of

molybdenum at the fuel surface is scattered more so than that at the center. The oxidized molybdenum was assumed to be dissolved in the oxide fuel matrix. This is a result of a fission process because oxygen cannot be completely bonded by the generated fission products. Hence, the ratio of the molybdenum concentration in the alloys to the MoO<sub>2</sub> concentration in the fuel matrix is an indicator of a local oxygen potential of a fuel which is based on an equilibrium state [5];

$$[\text{Mo}]_{\text{alloy}} + [\text{O}_2]_{\text{fuel}} = [\text{MoO}_2]_{\text{fuel}}. \quad (1)$$

Compositions of the precipitates observed at the grain boundaries and those of the intra grains were not different from each other. Namely, the concentrations of molybdenum and ruthenium tended to decrease as the  $r/r_0$  increased. The reason for this phenomenon is assumed to be the higher oxygen concentration at the periphery. Molybdenum and ruthenium elements are likely to be in the form of oxides when the concentration of oxygen is high. Because neutrons are generally absorbed in the fuel's surface region, which results in a higher fission rate there. Therefore, a higher oxygen concentration is maintained in the fuel surface region due to the liberated oxygen from UO<sub>2</sub> during nuclear fissions. The reason for a low concentration of molybdenum in the metallic precipitate in the fuel surface region is that molybdenum is likely to be an oxide of MoO<sub>2</sub> at a higher oxygen concentration. The oxidized molybdenum of a fission product is assumed to dissolve in a fuel matrix with an abundant amount of oxygen.

It was found that the concentration of Ru had a similar behavior of Mo with the same EPMA analysis methods. The data was also extracted by following the same procedure for Mo in Fig. 1(b). When considering a low burnup of the irradiated simulated fuel, it is understood that the precipitates of the perovskite phases are developed during the fabrication process of the irradiated simulated fuel (oxide/reduction, slitting process). A ceramic nucleation cluster may develop during a sintering process and a solid solution diffusion process. Therefore, it is understood that the main reason for a size change of the metallic precipitate at different regions is its various formations at different temporal conditions during an irradiation in the HANARO.

Fig. 1(d) depicts a projection of the radial concentration change for the metallic precipitate section of the Molybdenum-Ruthenium-Palladium phase diagram at 1700 °C [6-7]. At the regions of  $r/r_0 = 0.4$  and  $r/r_0 = 0.8$ , the phase of the lattice parameter was identified as  $\sigma+\epsilon$  phases and the others were  $\epsilon$  phases.



palladium and molybdenum than the usual precipitates. From Fig. 2, it is observed that a large metallic inclusion did not form a spherical shape. This abnormal shape might be due to a temperature distribution in the pellet during an irradiation. In the outer region of the inclusion, Pd and Ni are dominant, while in the center region, Mo and Ru are dominant. It is also noted that Fe, Ni, Cr were found in small amounts, which were initially introduced during the milling process of the simulated fuel. But the quantity of those impure isotopes such as Fe, Ni, Cr is not insignificant and it seems that the major metallic precipitate isotopes are widely scattered in the abnormal inclusion. It is also understood that impurities have different phases during an irradiation and that metallic precipitates accumulate around the impurities. However, more investigations should be undertaken not only by detailed a post-irradiation test but also by using various kinds of specimen fuels.

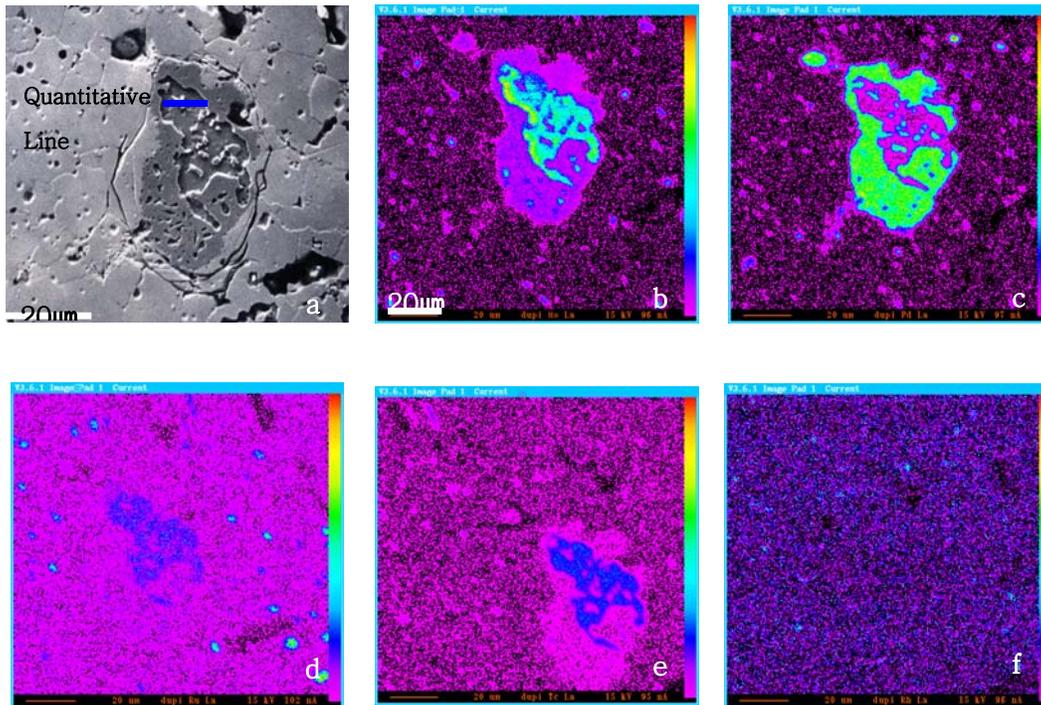


Fig. 2 Secondary image photomicrograph and Characteristic X-ray photographs ( $r/r_0=0.3$ ): (a) microstructure, (b) Mo L $\alpha$ , (c) Pd L $\alpha$ . (d) Ru L $\alpha$ . (e) Tc L $\alpha$ . (f) Rh L $\alpha$ .

#### 4. Conclusion

A detailed analysis was performed for the metallic precipitates of an irradiated simulated fuel and the results were compared with those of a fresh simulated fuel. From the results, it was suggested that the metallic precipitate was formed during the fabrication process of the simulated fuel because the irradiation period was not long enough in the HANRO test reactor. The oxidation and reduction processes had an effect on the formation of the metallic precipitates. Also a large metallic inclusion was found and some quantitative results are provided including the weight percentage for some major elements. To establish more reliable results for a metallic precipitate and a large metallic inclusion in an irradiated simulated fuel, more post-irradiation tests should be performed with various kinds of fuels. It is believed that the approach of this study will be helpful for analyzing the performance of impurities in an irradiated fuel.

## References

1. M.S. Yang, B.B. Kim, S.S. Kim and I.H. Jung, Proc. of the Int. Conf. on Future Nuclear Systems : Global 99, Jackson Hole, Wyoming, USA(1999).
2. J.D. Sullivan, P.G. Boczar, D.S. Cox, P.J. Fehrenbach, M.S. Yang and J.S. Lee, Proc. of the Int. Conf. on Future Nuclear Systems : Global 99, Jackson Hole, Wyoming, USA(1999).
3. I.H. Jung, K.C. Song, K.H. Kang, B.O. Yoo, Y.H. Jung and M.S. Yang, J. Metal. Mater. 5 (2001) 513.
4. H. Kleykamp, J.O. Paschoal, R. Pejsa, F. Thommler, J. Nucl. Mater. 130(1985) 427.
5. I. Jonson, C.E. Johnson, C.E. Crouthamel, C.A Seils, J. Nucl. Mater. 48(1973) 21.
6. H. Kleykamp, J.O. paschoal, R. Pejsa, F. Thommler, J. Nucl. Mater. 130(1985)431.
7. P.G Luctuta, R.A. Verral, Hj. Matzke and B.J. Palmer, "Micro Structural Features of SIMFUEL", J. Nucl. Mater. 179(1991) 48.