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Journal of Nuclear Materials 247 (1997) 46–49

journal of nuclear materials

Section 2. Fission products behavior

Distribution of molybdenum in FBR fuel irradiated to high burnup

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Abstract

Molybdenum is one of high yield fission products and has a chemical affinity for oxygen in uranium–plutonium mixed oxide fuel. In this work, radial distributions of molybdenum were investigated in high burnup fuels irradiated up to 13.33 at.%. It is found that the distributions are different from those expected from diffusion process in low burnup. This suggests that molybdenum in high burnup fuel migrates by not only a diffusion process but also by a gaseous molybdenum transport mechanism. © 1997 Elsevier Science B.V.

1. Introduction

The behavior of solid fission products in irradiated oxide fuel has a strong effect on the availability of oxygen that determines the oxygen potential and influences fuel swelling and thermal properties such as thermal conductivity and the melting point. Among a number of solid fission products, molybdenum of over 20% fission yield exists in chemical states of both the element and oxygen compound. Although the distributions of molybdenum in irradiated fuels have been reported in previous papers [1–4], the data in high burnup fuels are few so that a detailed discussion of molybdenum behavior was difficult.

In this work, radial distributions of molybdenum were measured in irradiated fuels and the profiles of the oxygen potential were derived by the reduction–oxidation (REDOX) method. The migration behaviors of molybdenum and oxygen were discussed.

2. Experimental

Radial distributions of molybdenum were measured in specimens taken from the top, middle and bottom of two fuel pins irradiated in the experimental fast reactor, JOYO. The as-fabricated characteristics and the local irradiation conditions are listed in Table 1. Cladding tubes of these pins were modified-316 stainless steel, Fe–16Cr–14Ni–0.05C–2.5Mo–0.7Si–0.025P–0.004B–0.1Ti–0.1Nb, and were 20% cold-worked [5].

Distributions of molybdenum on the cross section of fuel specimens were measured with an electron-prove microanalyzer attached to a hot cell of the fuels monitoring facility (FMF) at the Power Reactor-Nuclear Fuel Development Corporation. Molybdenum concentrations were derived from intensity of molybdenum Lα detected with PET as a spectrometer crystal. The acceleration voltage and the absorption current were 25 kV and 0.1 μA, respectively. A part of the molybdenum generating in fuels is present as a constituent of metallic fission product inclusions which consist of technetium, ruthenium, palladium, rhodium, etc. [6,7] and another part is present as solute in the urania–plutonia solid solution. The chemical equilibrium of molybdenum which is assumed to exist at each position in the fuel is as follows:

$$\text{Mo (in metallic inclusion)} + O_2 = MoO_2 \text{ (in fuel matrix)}. \quad (1)$$

In order to evaluate the oxygen potential with REDOX method similarly done by Johnson et al. [2], molybdenum

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0022-3115/97/$17.00
PII S0022-3115(97)00062-7

Table 1
As-fabricated characteristics and irradiation condition of fuel specimens

Pin no.	Specimen no.	Fractional location from fuel column bottom	As-fabricated characteristics				Local irradiation condition		
			Pu/(Pu + U)	density (%TD)	O/M ratio	diameter (mm)	linear heat rating at EOL (kW/m)	burnup (at.%)	cladding inner surface temperature (K)
G305	G30522	0.07					20.4	9.34	683
	G30561	0.50	0.3	85.2	1.95	5.408	25.8	11.97	765
	G30582	0.96					15.6	7.57	809
G357	G35722	0.07					20.9	10.37	695
	G35751	0.50	0.3	84.6	1.94	5.415	26.4	13.33	791
	G35782	0.96					16.4	8.39	851

had to be analyzed in both metallic inclusions and fuel matrix.

3. Result

Fission product metallic inclusions were metallographically observed on the cross sections of all specimens. The radii of inclusions near a fuel central void were about 7–9 μm. On the other hand, the geometric sizes of inclusions at the unrestructured region were smaller, especially these radii near the fuel outer surface were less than 1 μm.

Fig. 1 shows the distribution of the molybdenum concentration in metallic inclusions and the fuel matrix as a function of fuel relative radius. Molybdenum concentration in inclusions near a central void is higher than that in inclusions near the fuel surface. On the other hand, radial distributions of molybdenum in the fuel matrix show the opposite tendency to ones in inclusions. It is, however, noted that molybdenum concentrations in both phases are generally higher in the low burnup fuel than in the highest burnup fuel.

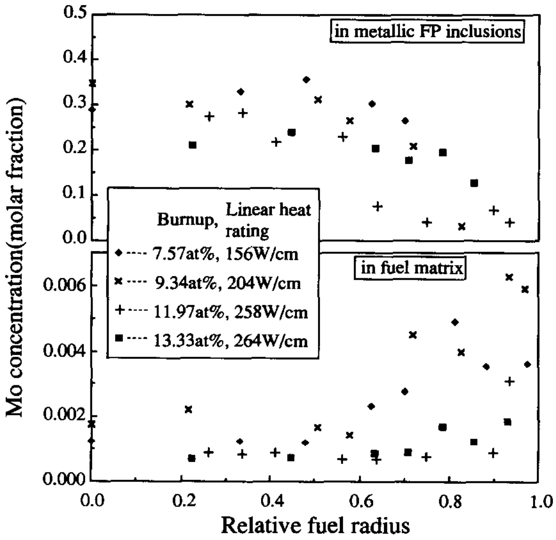

Fig. 1. Distribution of molybdenum concentration versus relative fuel radius in white metal phase and fuel matrix.

4. Radial profiles of oxygen potential in fuels

When the law of mass action is applied to Eq. (1), oxygen potential in a fuel is obtained,

$$\Delta\overline{G}_{O_2} = \Delta G^{f}_{MoO_2} + RT \ln\left(\frac{a_{MoO_2}}{a_{Mo}}\right), \tag{2}$$

where $\Delta\overline{G}_{O_2}$, $\Delta G^{f}_{MoO_2}$, R and T are oxygen potential (J/mol), standard free energy of formation of molybdenum dioxide (J/mol) that was referred from a literature [8], gas constant (J/(K mol)) and fuel temperature (K), respectively. a_{MoO_2} and a_{Mo} are activities of molybdenum dioxide in fuel matrix and of molybdenum in metallic inclusions. These activities were calculated by a method that was adopted by Johnson et al. They derived activities

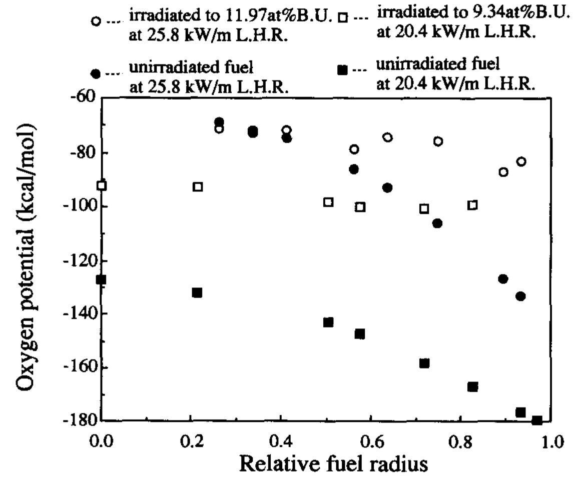

Fig. 2. Oxygen potential versus relative fuel radius for fuels unirradiated, and irradiated to 11.97 and 9.34 at.% burnup.

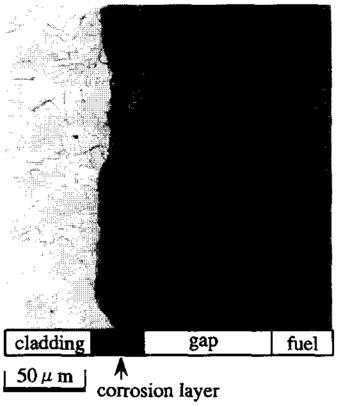

Fig. 3. Corrosion layer of the cladding inner surface of the 7.57 at% fuel, G30582.

in inclusion and matrix from an assumption, in which metallic inclusions and fuel matrix formed regular solution with molybdenum.

Radial profiles of fuel temperature for specimens were obtained with one dimensional thermal conduction equation.

Fig. 2 shows that radial profiles of oxygen potential for two specimens, G30522 and G30561, irradiated to 9.34 and 11.97 at.%, respectively. Oxygen potential for unirradiated MOX fuel can be estimated from fuel temperature, initial O/M ratio and Pu content [9]. The profiles of oxygen potential of unirradiated fuel were calculated under the temperature condition of corresponding irradiated specimens and are also shown in Fig. 2. It is assumed in this analysis that O/M ratio remains unchanged as shown in Johnson's works [2]. The comparison of profiles of oxygen potential for G30522 shows that the oxygen potential increases with burnup. This arises from excess oxygen by fission.

Johnson et al. [2] have reported that oxygen potential for a fuel irradiated to 6.5 at.% burnup at 525 W/cm linear heat rating was lower than that before irradiation, which resulted in absorption of the excess oxygen on the cladding inner surface. The disagreement between this work and Johnson's result may be caused by the influence of the linear heat rating which leads to cladding temperature. The linear heat ratings in this work were about half of the irradiation condition of Johnson's work. Fig. 3 shows the metallography of a fuel-cladding gap of G30582 where the thickest corrosion layer in the fuel pin was observed. The cladding inner surface corrosion is about 30 μm at most in this specimen. Corrosion layer was not observed in other specimens. This fact indicates that the cladding tube used in this work does not absorb excess oxygen so much. As shown in Fig. 2, oxygen potential near a central void for G30561 has not changed between the irradiated and the unirradiated case. This suggests that oxygen in high burnup fuels at higher temperature region can migrate to lower temperature region significantly.

5. Discussion

Figs. 4 and 5 show the comparisons of temperature dependence of molybdenum concentrations in between present results and previous results by Johnson [2]. The burnups of the specimens are classified into 3 groups, that is, the lower burnup is less than 7 at.%, the medium burnup is between 7 and 10 at.% and the higher burnup is between 10 and 14 at.% burnup. In Fig. 4, the molybdenum concentration in the lower burnup group is higher than in other two groups, and the concentration in the higher burnup group is lowest. In contrast to this, molybdenum distribution in fuel matrix does not distinct burnup dependence, as shown in Fig. 5. In high burnup group, the concentration in the fuel matrix is low as similar as in metallic inclusions. This indicates that total molybdenum content in the higher burnup group decreases from that in the lower group.

Fig. 6 shows a EPMA result, which indicates the existence of molybdenum in the fuel-cladding gap of the specimen irradiated to 11.97 at.% burnup. This suggests that molybdenum releases from the fuel outer surface. According to understanding of molybdenum diffusion behavior [10], molybdenum diffusion coefficient in oxide fuel is very small. Therefore, no significant amount of molybdenum is expected to migrate by diffusion from inner to outside in the fuel.

Johnson et al. suggested that molybdenum migrates as gaseous Cs_2MoO_4 at low temperature and high oxygen potential [11]. Kleykamp also suggested that migration chemical form of molybdenum was MoO_3, considering instability of Cs_2MoO_4 at high temperature and under the

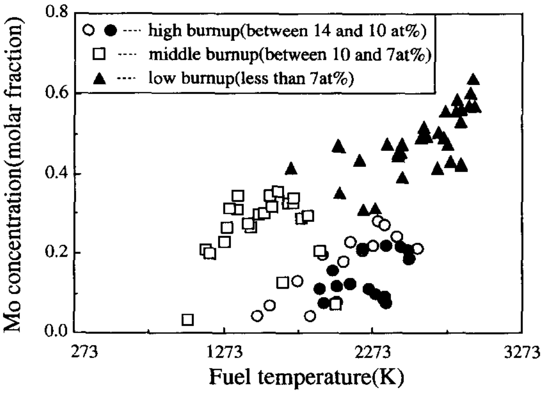

Fig. 4. Molybdenum concentration in FP metallic inclusions versus fuel temperature: Open symbols in this study; Solid symbols in Johnson et al. work [2].

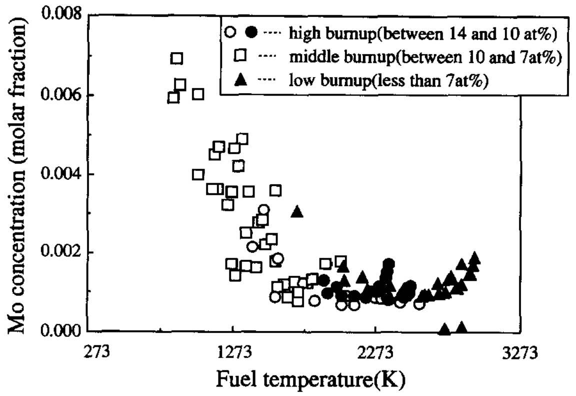

Fig. 5. Molybdenum concentration in fuel matrix versus fuel temperature: Open symbols in this study; Solid symbols in Johnson et al. work [2].

influence of the radiation field [12]. If molybdenum can migrate as Cs_2MoO_4 or MoO_3, it is expected that oxygen can move from hotter region to colder region simultaneously. As shown in Fig. 2, although more excess oxygen can be generated in high burnup fuel than in lower ones, the oxygen potential near the central void did not change between unirradiated and the fuel irradiated to 11.97 at.% under the same temperature condition. It is possible that oxygen in the high burnup fuel migrates more easily than that in low burnup. Molybdenum migration may influence oxygen re-distribution in high burnup. Models of oxygen re-distribution in fuel during irradiation are based on counter-diffusion of contamination such as hydrogen and carbon oxide, or thermal diffusion of oxygen [13,14]. Moreover, the heat of transport in thermal diffusion of oxygen used in the models is measured in fresh fuels. The effect of burnup may be taken into consideration when oxygen re-distribution in high burnup fuel is treated, because of gaseous migration of molybdenum-oxides compounds.

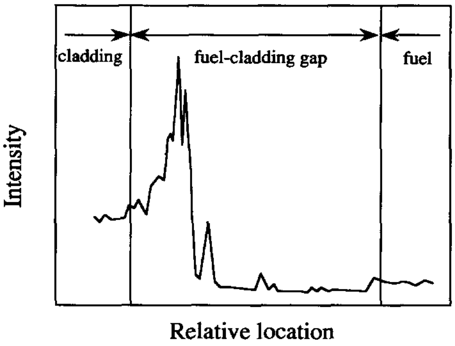

Fig. 6. A EPMA line analysis of molybdenum in the fuel-cladding gap of the 11.97 at.% burnup fuel.

6. Conclusion

Radial distributions of molybdenum were measured in fuel specimens irradiated to high burnup. The concentration of molybdenum in the higher burnup fuel is lower than that in the lower burnup fuel. Significant amount of molybdenum was found in fuel-cladding gap of a high burnup fuel. These distributions suggest that molybdenum probably releases out of high burnup fuel through transport of gaseous molybdenum-oxide compounds. The profiles of oxygen potential suggest that this gaseous transportation may influence oxygen re-distribution in high burnup fuels.

Acknowledgements

The authors are grateful to Mr Y. Ohsato, Mr Y. Onuma and Mr S. Nukaga (Nuclear Engineering Corporation) for help with the experiments.

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