Migration of minor actinides and lanthanides in fast reactor metallic fuel

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ABSTRACT

Minor actinides (MA) and lanthanides (LA) migration to the cladding in fast reactor metallic fuel is a concern because of their reaction with the cladding material. MA and LA migration test results are analyzed and reactions with the cladding are characterized. Remedies for reducing MA and LA migration and reaction with cladding are reviewed. A possible method is proposed that includes the addition of a compound forming element such as indium or thallium in fuel. These elements preferentially form stable compounds with MA and LA and should therefore reduce migration of MA and LA. As an intrinsic solution to the issue, the feasibility of the use of U–Pu–Mo alloy as fuel is studied. Unlike U–Pu–Zr, U–Pu–Mo consists of a single phase at typical fuel operation temperatures, and should have negligible fuel constituent redistribution and reduce MA and LA migration.

1. Introduction

In minor-actinide burning reactors such as proposed for the GNEP system, redistribution of minor actinides (MA = Np, Am, Cm, etc.) is of concern due to their potential to react with cladding. The reaction of MA with cladding leads to wall thinning and reduction in cladding melting point. More significantly, if MA react with cladding, the cladding must be subject to reprocessing, which increases the overall fuel reprocessing cost.

Although metallic fuel irradiations in the EBR-II reactor have accumulated abundant data, irradiation experience of MA-included metallic fuel is rather limited because the concept of burning MA in a fast reactor has only been introduced relatively recently. Data from experiments such as the X501 test from the IFR program have shed some light on this subject [1,2].

Lanthanides (LA = La, Ce, Pr, Nd, etc.) also accumulate as fission products in the fuel. LA are reactive with stainless steel cladding and the reaction products lower the cladding melting point. Some of them appear to have similar migration behavior as MA. Therefore, test data with LA provide valuable insight in predicting the behavior of MA-bearing fuel. In particular, considering the high cost and difficulty of dealing with actinides, the use of surrogate LA seems practical. For example, Sm has a vapor pressure higher than Am, which has the highest vapor pressure among MA. A further study that accounts for feasibility and thermodynamics, however, is required to identify adequate candidates.

In this paper, we present test results for migration behavior of MA and LA in U–Pu–Zr. The test results of high temperature reaction between fuel and cladding are also presented. The LA reaction with cladding, as well as MA reaction with cladding, are also analyzed.

The existing remedy for preventing MA and LA interaction with fuel element cladding is to install a diffusion barrier on the cladding inner surface. Some alternative methods are proposed here.

2. MA and LA migration

Only a limited amount of information on irradiation experience with MA bearing U–Pu–Zr is available. The WDS (wavelength dispersive spectroscopy) measurements of the G582 fuel element from the EBR-II X501 test is shown in Fig. 1. The fuel was fabricated by adding 2.1 wt% Am and 1.3 wt% Np in U–20Pu–10Zr and was irradiated to a burnup of ~6 at% at the peak fuel centerline and surface temperatures of 700 and 540 °C, respectively. The irradiation achieved 9.1% transmutation of Am. The WDS measurements show typical U, Pu, and Zr redistribution (for more details, see for example Refs. [1,2]), and Am is found mainly in precipitates in the regions where large pores were observed. However, Np is more uniformly distributed, much like Pu.

In previous models [1,2], Am migration behavior was explained by a mechanism in which Am vapors move through interconnected pores down the radial temperature gradient. This mechanism relies on the observation that Am was located mainly where large interconnected pores were available.

However, it is also easier for Am atoms to precipitate in the pores than in the fuel matrix because Am has limited solubility in U–Pu–Zr alloy. In addition, the vapor transport mechanism cannot explain the observation that Am precipitates are also found in the fuel region where the temperature is higher than in the fuel periphery region. Thus, Am interdiffusion through the fuel matrix and subsequent precipitation in the pores appears to be more

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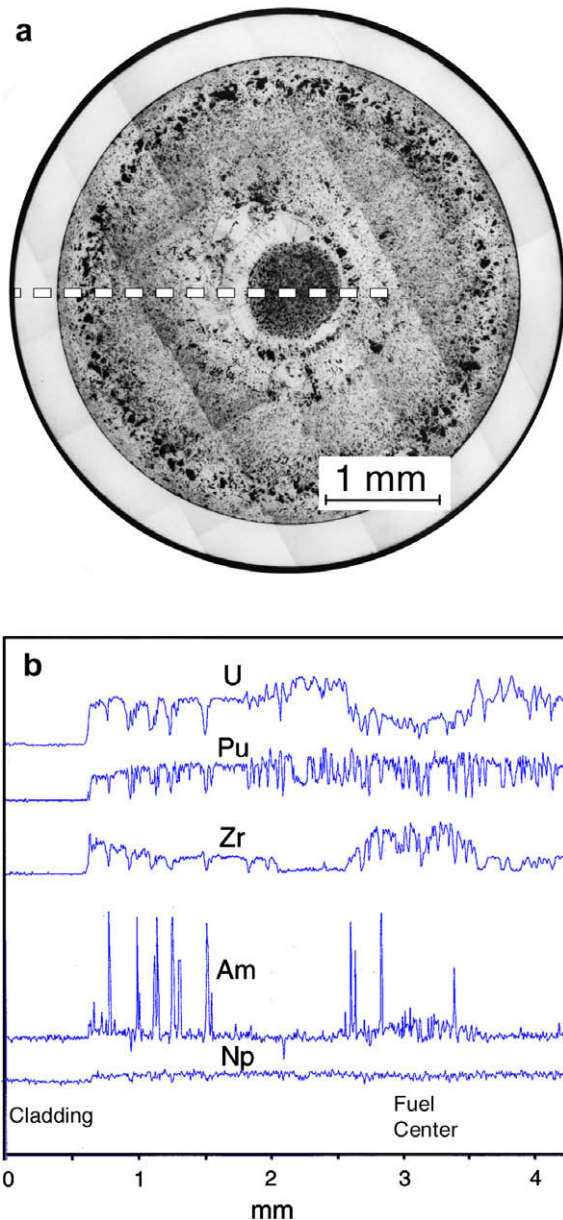
Fig. 1. (a) Optical micrograph of the fuel cross section of G582 from X501 test, (b) WDS data showing concentration redistribution, along the scan direction indicated by the broken line in (a).

plausible. The migration mechanism is probably complex, involving some vapor transport and surface diffusion in interconnected pores in addition to interdiffusion in the fuel alloy.

The DP-11 fuel element from the X447 test contained U–10Zr and was irradiated in EBR-II to peak burnup of 10 at% at the fuel centerline and the surface temperature 820 and 660 °C, respectively. Fig. 2 shows the cross section of DP-11 at axial elevation of 0.93 z/L [3]. As shown, there is noticeable zone formation in fuel. Because of high temperature irradiation, some of the fuel had reacted with the HT9 cladding. Two Electron Probe Micro Analysis (EPMA) scans were made: one, across the fuel cross section for fuel constituent redistribution and lanthanide migration; and the other, at the area of fuel-cladding interaction. These EPMA results are shown in Figs. 3 and 4, respectively.

The fuel temperatures of DP-11 are ~100 °C higher than those of G582. The DP-11 was tested at a higher-than-typical temperature to obtain a margin in temperature with respect to LA migration and reaction with cladding. DP-11 is believed to have faster

LA migration than more typical, lower temperature tests such as G582. The reaction between LA and the cladding observed in DP-11 is a direct effect of the high temperature.

Like U–Pu–Zr, U–10Zr formed zones because of constituent redistribution. The zone average Zr concentration varied from 30 wt% in the central zone to 2 wt% in the intermediate zone and to 10 wt% in the peripheral zone. As shown in Fig. 3, the redistribution profiles of LA have large spikes. More spikes are seen at the fuel periphery region than the fuel center region, which is similar to the behavior of Am in U–Pu–Zr. The spike strength of Sm is weaker than those of La, Ce, Pr, and Nd because of its lower concentration. The uranium fission yield fractions for LA are 0.18 for Nd, 0.17 for Ce, 0.06 for La, 0.05 for Pr, and 0.02 for Sm.

Np and Pu are mutually soluble and both sessile, and show similar migration behavior. Np can be treated as Pu as far as migration is concerned. No test result with Cm is available. Since the yield of Cm is small, the equilibrium concentration of Cm is less than Am and Np. Because Cm is more similar to Am and LA, Cm is expected to have similar behavior to Am and LA. Like LA, the solubility of Am in U, Pu or Zr is very low. Am and LA migration behavior may be generally similar. According to Johansson's correlation [4], Am is close to Pr and Nd in chemical and structural properties, suggesting an analogous behavior in migration of these elements.

3. MA and LA reaction with cladding

Fig. 5 shows that LA precipitated in pores in U–Pu–Zr near the HT9 cladding inner surface. It is probable that the cross section shows no sign of fuel-cladding interaction because the cross section was taken from an axial location closer to the fuel bottom where fuel temperature and burnup were relatively low. Two kinds of LA compounds were observed in Fig. 5; one brighter, the other darker on the optical micrograph. The dot maps measured for DP-11 test, given in Fig. 6, show that there are indeed two kinds of compounds. The Nd rich phase appears to include Pr, La, and Ce, taking the broadest area. Ce also exists with Pr, La, and Nd. The area taken by Ce is narrower than that of Nd, suggesting that LA form two kinds of compound, one with Nd-rich, Nd–Pr–La–Ce, and the other Ce-rich Ce–Pr–La–Nd. We also observed that LA reaction behavior with cladding in U–19Pu–10Zr, although not shown here, is the same as in U–10Zr.

From the DP-11 test, LA showed reaction with the cladding at higher temperatures as shown by the EPMA profiles in Fig. 4. It is also remarkable that only LA reacted with cladding while U and Zr stayed in the fuel, not penetrating the cladding. LA were found in the cladding and cladding constituents were found in the fuel, suggesting the reaction was by way of interdiffusion between LA and cladding constituents. All LA seem to have reacted with the HT9 cladding. Nd and Ce, having the highest yields, accumulated the most in the cladding. Among the major cladding constituents (Fe, Cr, and Ni), Ni penetrated the farthest into the fuel. This is due to Ni affinity for LA, which is higher than Fe and Cr. This observation is consistent with the test result by Sari et al. [5], which showed that Ni forms a compound with Am and LA.

As discussed in Section 2, the DP-11 was an elevated temperature test that has the fuel and cladding temperatures ~120 °C higher than G582. This caused the enhanced interdiffusion between LA in the fuel and the constituents of the cladding. For more typical test pins, reaction between the fuel and cladding is not usually observed.

There is no experimental data for the reaction between MA and cladding. The paucity of fundamental information does not encourage a theoretical prediction either. However, considering the similarities between LA and Am, Am also will likely react with HT9 cladding. This hypothesis can only be confirmed by further tests.
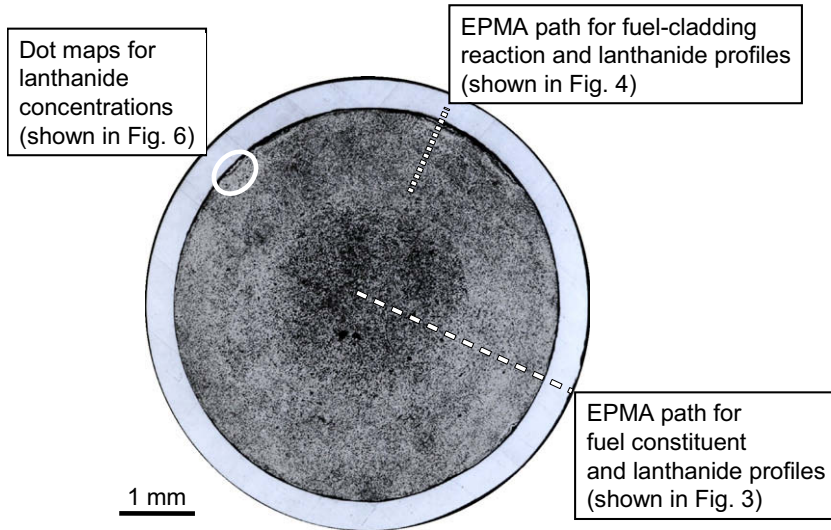
Fig. 2. Cross section of DP-11 from X447 irradiated in EBR-II to a burnup of 10 at% at cladding temperature 650 °C.
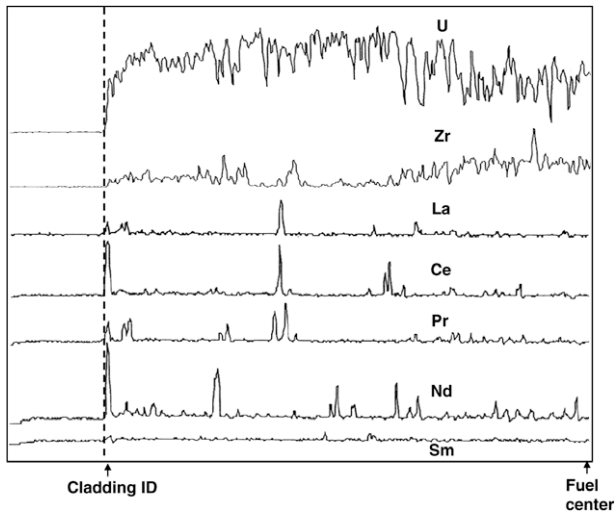

Fig. 3. U, Zr and lanthanide redistribution profiles in irradiated U–10Zr fuel of DP-11 pin in X447 irradiated in EBR-II. The EPMA path is shown in Fig. 2.

4. Remedies for MA and LA migration

4.1. Placing a diffusion barrier for MA and LA

The idea to use a diffusion barrier stemmed from the tests of a vanadium liner with type 304 austenitic stainless steel (304 SS) and tungsten liner with Hastelloy-X (nickel alloy) at Argonne National Laboratory [6]. It also originated from the use of vanadium alloys as cladding, and the use of tungsten as the liner material on cladding in space reactor fuels. A thin (~100 μm) vanadium liner on the inner surface of HT9 cladding was tested as a protection for the cladding from LA attack [7]. The test results, however, were not promising because the failure rate with a cladding liner was unacceptably high (i.e., ~9 out of 12 tests). Undetected defects in the liner were the main cause for the failures. In general, difficulties were encountered in obtaining duplex cladding that had a uniform layer of liner cladding free of pinhole
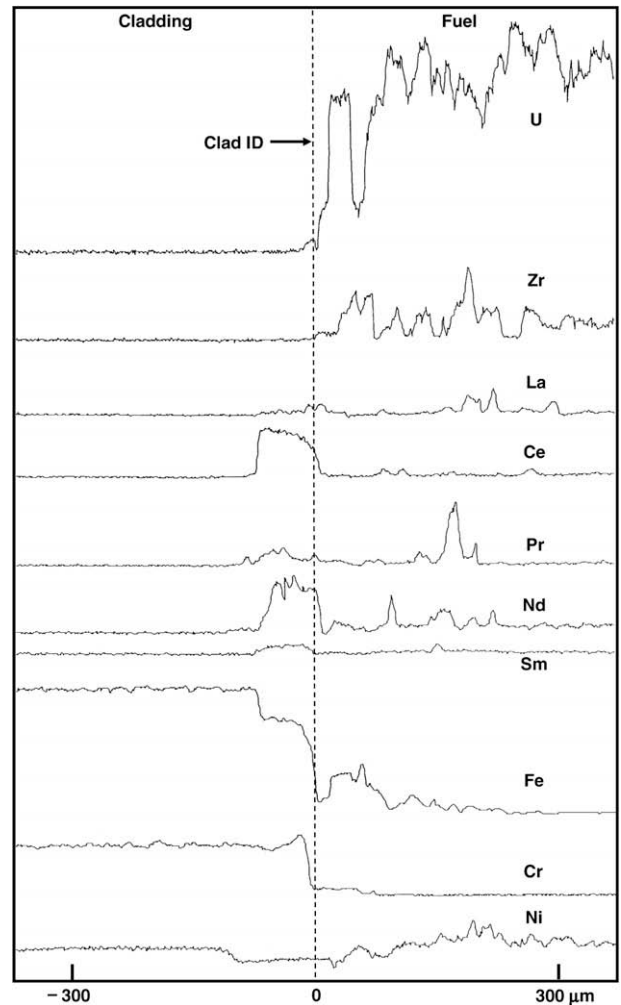

Fig. 4. EPMA concentration profiles of LA compared to fuel constituents and cladding constituents showing reaction with HT9 cladding of DP-11 pin at the reaction zone shown in Fig. 2.
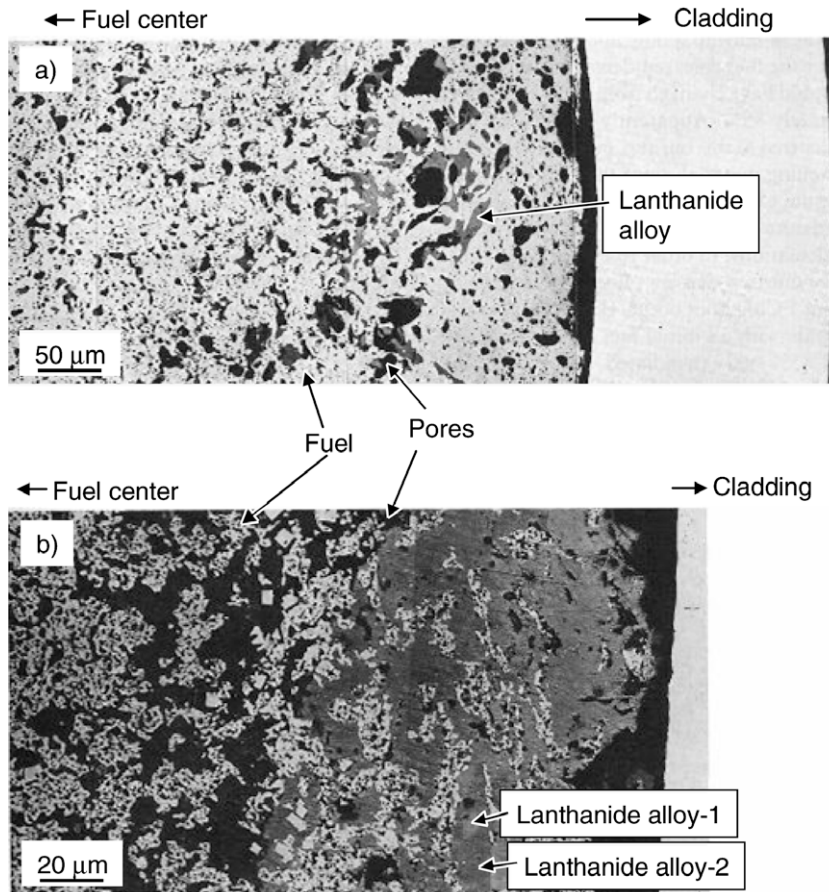
Fig. 5. Optical micrographs showing the cross sections: (a) medium-burnup U–19Pu–10Zr fuel near cladding, (b) high-burnup U–19Pu–10Zr fuel near cladding.
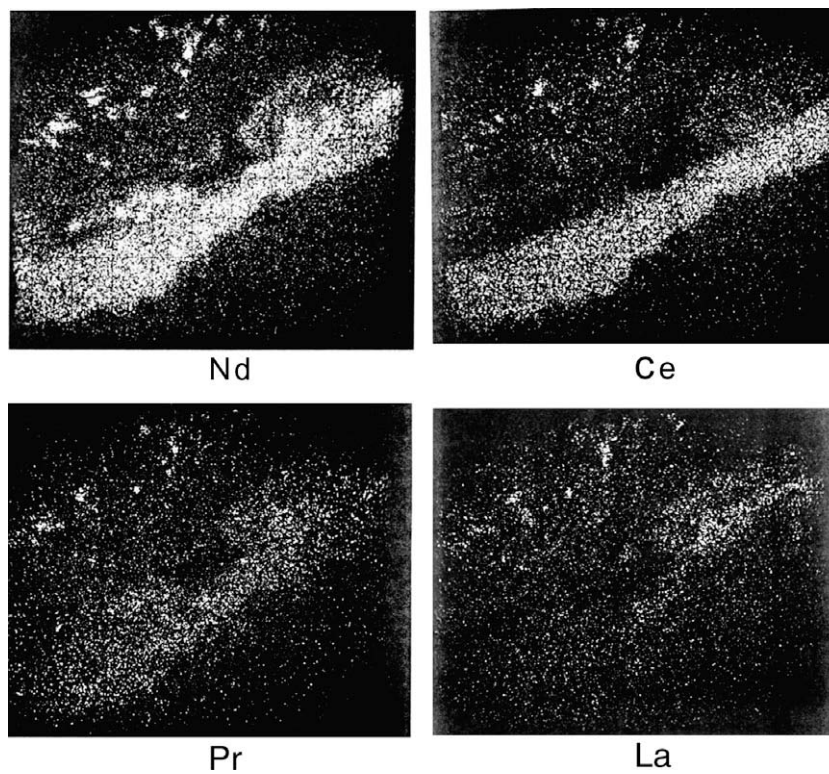

Fig. 6. Dot maps for LA concentrations at the reaction zone with cladding shown in Fig. 2.

defects. Another method was to put a Zr-barrier on the U–Pu–Zr fuel during alloy casting, which was advantageous due to the use of a Zr liner tube as the mold during injection casting. However, because of high fuel-cladding chemical interaction, the irradiation test to 2 at% burnup found no beneficial effect of 0.2-mm thick Zr-liner on 316 SS cladding [8].

However, there have been successful attempts in recent years to apply barrier materials on the inner surface of the cladding that make the barrier coating method more viable (see Ref. [9] and references therein). Several methods to apply uniform barrier coating on the inner surface of the cladding have been developed. Nonetheless, in order to obtain a quality coating, an increase in fuel fabrication cost is inevitable. There is also the possibility of degradation of the barrier by mechanical and chemical interaction with fuel.

4.2. Immobilizing LA and MA

Migration of MA and LA may be stopped by adding a thermodynamically stable compound-forming element such as indium or thallium to the fuel. Fig. 7 compares the compound formation enthalpies of In with fuel and cladding constituents. The low (i.e., negative) enthalpies of formation of In with all LA relative to fuel constituents imply that In will preferentially form compounds with the LA. LA may thereby be immobilized in the fuel matrix. The positive enthalpies of formation of In with Fe and Cr predict that In will not react with cladding.

As shown in Fig. 8, Tl also shows a behavior similar to In. It has positive enthalpies of formation with cladding constituents, slight negative enthalpies of formation with fuel constituents, and large negative enthalpies of formation with LA.

Since Ga is known to stabilize Pu and is positioned in the same group as In, it may also be a good candidate for this purpose. However, Ga will form stronger compounds with Zr than with LA. In addition, Ga reacts with all cladding constituents. Thus, Ga seems to be less attractive than In and Tl.

The main advantage of this method is that it potentially stops LA migration by way of a chemical reaction rather than by a passive method such as the cladding liner. Therefore, the quality control should be easier than the liner method, and the stopping power for LA migration is not degraded with burnup. Above all, this method does not increase cladding thickness. More fuel development time would be needed for this method.

The combined yield of all LA fission products is approximately 50% per fission, which gives 3.6 at% LA concentration at 20 at% bur-
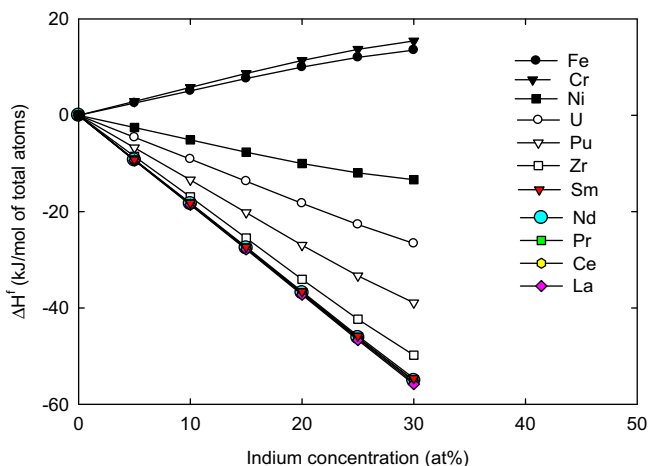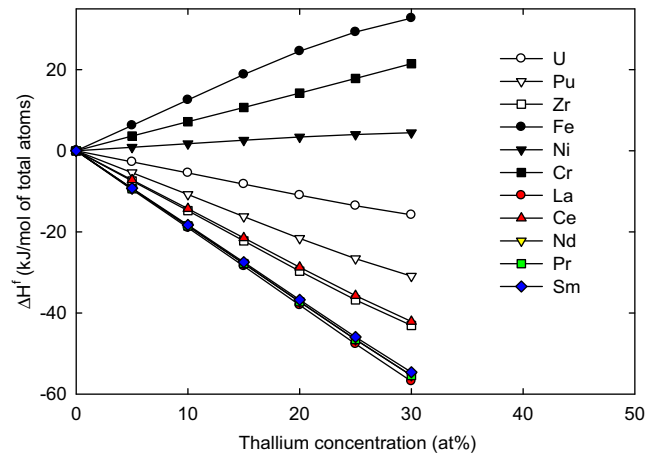

Fig. 8. Enthalpies of formation of Tl-X compounds estimated using the Miedema model [17].

nup in U–10Zr fuel. For all LA, indium forms $LAIn_3$, $LAIn_2$, $LAIn$, LA_2In, and LA_3In type compounds. On average, 7.2 at% (or 4.4 wt%) In is needed to immobilize the LA. Similarly, 7.2 at% (or 7.4 wt%) thallium is needed because it has similar behavior to indium as to compound formation. For MA bearing U–10Zr fuel, no additional amount of In or Tl is necessary to immobilize MA because the In- or Tl-MA compounds will free In or Tl during MA fission.

Indium and thallium have an absorption cross section of ~1.7 barns for 14 MeV neutrons, as low as Zr, so any effect on the fuel neutron economy should be negligible.

4.3. Using a different fuel alloy

As evidenced in X501 test results, MA and LA migration appears closely connected to fuel constituent redistribution and zone formation. Therefore, if fuel does not undergo constituent redistribution and zone formation, MA and LA migration should be reduced.

In U–Zr and U–Pu–Zr, fuel constituent migration occurs at the normal fuel operating temperature regime. Moreover, in U–Pu–Zr, the redistribution kinetics increases as the Pu composition increases.

As shown in Fig. 9, U–Pu–Zr alloy extends over three phase fields in the temperature range 580–750 °C. Since the driving force for constituent redistribution stems from the difference
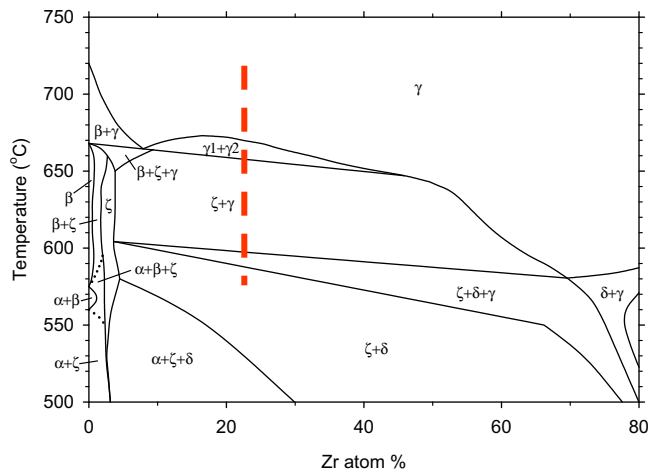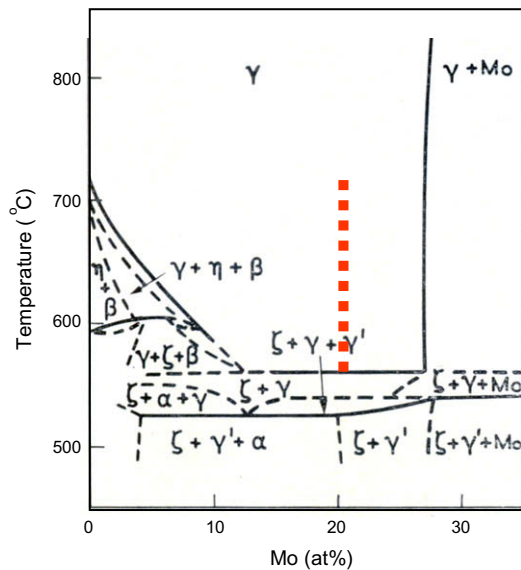

Fig. 7. Enthalpies of formation of In-X compounds estimated using the Miedema model [17].

Fig. 9. Pseudo-binary phase diagram of U–Pu–Zr at 19 wt% Pu [21]. The vertical broken line represents for U–19Pu–10Zr in weight% (i.e., U–16Pu–22Zr in at%) over a typical fuel operating temperature range.

Fig. 10. Isopleth of U/Pu ratio 3 [22]. The vertical broken line indicates the phase field at which U–19Pu–10Mo exists at typical fuel operation temperatures.

in thermochemical properties between the adjoining phases in fuel, U–Pu–Zr fuel is most prone to exhibit constituent redistribution and radial zone formation.

In contrast, U–Pu–Mo alloy in the temperature range 550–950 °C only exists in the single γ phase field, as shown in Fig. 10. In this single phase, large chemical potential differences that drive constituent migration and zone formation are absent, and, by inference, lower migration of MA and LA in the radial temperature gradient. Vapor transport and surface diffusion in the developing interconnected porosity would still be a possible mechanism for radial migration of LA and MA, however.

The thermal properties of U–Pu–Zr and U–Pu–Mo are compared in Table 1. Thermal conductivity and thermal expansion of U–Pu–Mo are somewhat better than U–Pu–Zr. U–Pu–Mo has a slightly higher melting point than U–Pu–Zr. Both alloys have similar heat capacities.

U–Pu–Zr has an advantage over U–Pu–Mo fuels in cladding compatibility. The reaction rate of U–Pu–Zr fuel with 304 SS cladding is higher than U–Pu–Mo. The melting temperature of the reaction products between U–15Pu–10Zr alloy and 304 SS is 805 °C [18,19], which is also better than other metallic fuels. The superior cladding compatibility of U–Pu–Zr with Fe-base cladding is fortuitously due to Zr accumulation at the cladding inner surface. This Zr accumulation at the fuel cladding inner surface increases the fuel-cladding eutectic point because the eutectic temperatures between Zr and the constituents of Fe-base cladding are higher than those between U and Pu and the constituents of Fe-base cladding. Zr migration to the cladding is due to its high affinity for nitrogen and oxygen that are dissolved in stainless steel.

A U–12Pu–9Mo test against 304 SS at 650 °C showed reaction layer thickness of 20 μm, and addition of Mo in U–Pu decreased the reaction rate [20]. Although there is no cladding compatibility data for this alloy, an indirect comparison might be possible. In U–Pu–Fs alloy, Fs comprises 2.4 wt% Mo, 1.9 wt% Ru, 0.3 wt% Rh, 0.2 wt% Pd, and 0.1 wt% Zr of the fuel mix. The melting point of the reaction products of U–15Pu–10Fs with 304 SS was 650 °C [18]. The reaction products of U–19Pu–10Mo with 304 SS cladding is likely to be similar. From the standpoint of cladding compatibility, the U–Pu–Zr alloy has an advantage over U–Pu–Mo.

The use of molybdenum in LWRs suffers from high thermal neutron absorption ~7.5 barns for [95]Mo (natural abundance of 16 at%) and the transmutation of [98]Mo (natural abundance of 24 at%) to the long-lived radiotoxic [99]Tc [23]. In fast reactors, however, these problems do not exist because the fast neutron absorption cross section of all Mo isotopes are similar to those of Zr, and the amount of Tc produced from fission of the Pu in the U–Pu–Mo alloy fuel is orders of magnitude larger than the production of Tc from transmutation of [98]Mo. Therefore, replacing Zr with Mo has no radiological or neutronic disadvantage.

It is true that developing a new fuel alloy obviously takes more time. However, the advantages of the proposed fuel alloy are large enough to justify the additional fuel development effort and time.

5. Conclusions

Lanthanides (LA = La, Ce, Nd, Pr) show similar migration behavior to Am in U–Zr and U–Pu–Zr fuel. These elements commonly have very limited solubilities in U and Pu. The migration mechanism of LA and Am appears to depend primarily on interdiffusion in the fuel matrix and precipitation in pores. LA form two kinds of compounds that differ in Nd and Ce concentration. As U–Zr and U–Pu–Zr have similar fuel constituent redistribution and radial microstructural zone formation, then from a mechanism standpoint LA and MA migration behavior in U–Zr and U–Pu–Zr is also thought to be comparable. Np is inactive from the migration viewpoint. Am, though, would behave similarly to Pr and Nd.

The test with U–10Zr in HT9 cladding showed that LA reacted with cladding while U and Zr did not. This result led us to speculate that Am also will react with cladding in a similar fashion to LA.

Three kinds of remedies for reducing MA and LA migration are analyzed: (1) placing a diffusion barrier at fuel-cladding interface, (2) immobilizing MA and LA by adding a compound-forming element in fuel such as In or Tl, and (3) using U–Pu–Mo fuel instead of U–Pu–Zr. Option (1) received considerable attention in the past and showed promising results in recent studies. However, this method has disadvantages of high fuel fabrication cost and losing integrity of the barrier during irradiation by mechanical and chemical interaction between fuel and cladding. Option (2) uses a neutronically benign chemical additive in the fuel that does not lose effectiveness during irradiation. Fuel fabrication for this method is simpler than the option (1). From cost and performance point of view, this option is attractive and worth developing. Option

Table 1
Comparison of thermal properties of alloys.

	U–Pu–Zr			U–Pu–Mo
Thermal conductivity (W/m-K)	T (°C)	U–18Pu–11Zr (wt%)		U–20Pu–10Mo (wt%)
	500	19.3 [10]		21.6 [11–13]
	600	21.4 [10]		23.9 [11–13]
	700	23.2 [10]		24.1 [11–13]
	800	25.0 [10]		27.1 [11–13]
Melting point (Solidus) (°C)	1150 [14] for U–19Pu–10Zr			1175 [14] for U–19Pu–10Mo
Linear thermal expansion from 293 to 773 K (10^6)	17.3 [13] for U–20Pu–10Zr			16 [13] for U–20Pu–10Mo
Heat capacity at 500 °C (J/g-K)	0.2 [15] for U–15Pu–10Zr			0.17 [16] for U–20Pu–2.5Mo

Note: Numbers in the brackets [] are reference. Numbers in front of an element indicate weight%.

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(3) is metallurgically simpler than the other two options, but it will require more development effort and time because it involves changing the basic alloy from U–Pu–Zr to U–Pu–Mo. The irradiation database of the former is extensive.

Acknowledgments

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