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Review

Lanthanide migration and immobilization in metallic fuels

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ABSTRACT

It is recognized that the lanthanide fission products can enhance the fuel-cladding chemical interaction (FCCI), which is a key concern of using metallic fuels such as U-Zr in a sodium-cooled fast reactor. The present work conducts a critical review on the analysis of lanthanide functions in FCCIs. Available in-pile and out-of-pile data are first collected and analyzed, then the theories for lanthanide migration and redistribution in the fuel in operation are analyzed. For mitigating FCCIs, one of the effective method is applying fuel additives for immobilizing lanthanides. The review investigates four candidates of fuel additives (Pd, Sn, Sb and In), and it is concluded that Sb can be the best candidate among the four elements based on current available thermodynamic data and microstructure characterizations. Considering that FCCIs lead to formation of metallic alloys/compounds between lanthanides and steel cladding constituents (Fe, Cr, and Ni), the review also analyzes the thermodynamic data such as enthalpy of formation of the alloys and/or metallic compounds and identify the solidus temperature of each alloy.

1. Introduction

The selection by the Generation IV International Forum of sodium-cooled fast reactor concept has brought metallic fuels, such as U-Zr fuel, under renewed focus (Delage et al., 2013). Metallic U-Zr fuels have shown advantageous capabilities, including a high thermal conductivity, high fissile atom density, easy fabrication, and pyroprocessing capability. Along with these properties, metallic fuels have shown good performance on both steady state and transient operating conditions of sodium-cooled fast reactors by experiments performed with the experimental breeder reactor II (EBR-II) (Carmack et al., 2009). The metallic fuel pin is comprised of rod-shaped fuel alloy made of U-Fs,[1] U-Zr or U-Pu-Zr, the fuel-to-clad gap filled with liquid sodium (Na), and steel cladding HT9[2] (Carmack et al., 2009). The fuel pin is designed to allow for fuel swelling within the fuel-to-clad gap, and fission gas accumulating in the top plenum during reactor operation.

One of the earliest developments on metallic fuels was alloying. Some of the earliest alloying additions included molybdenum (Mo) and fissium (Fs). Later, Zr became the alloying element for metallic fuel in the use of EBR-II and fast flux test facility (FFTF) (Carmack et al., 2016). Alloying with Zr presents the ability to raise the solidus temperature of fuel, increase the compatibility between cladding and fuel, and increase the dimensional stability of metallic fuel under irradiation. It has been identified that the best composition of Zr is 10 wt. % in the fuel (Hofman et al., 1997). Although fuel alloying can increase the dimensional stability of metallic fuels under irradiation, design refinement of fuel element is still desired to reduce the effects of fuel swelling and chemical interactions between fuel and cladding.

At the beginning of metallic fuel development, the fuel-to-clad gap was relatively small, so large stresses were generated when fuel swells even at very low burnups (~3 at. %) (Pahl et al., 1992). Failures from the fuel imposing stresses on the cladding is known as fuel-cladding mechanical interaction (FCMI). To overcome FCMI, the designed thickness of fuel-to-clad gap was increased. The smear density was decreased to 75% to allow the fuel with more initial unconstrained swelling to prevent failures caused by FCMI (Hofman et al., 1997). With 75% smear density, an adequate amount of swelling occurs with the porosity developing in the fuel to form interconnected pathways from the fuel to the gap. The interconnected pathways allow fission gas to release from the fuel and to accumulate in the plenum at the upper

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[1] Fs (fissium) is composed of Ru, Mo, Pd, Te, Rh, Nb and Zr.
[2] Alloy HT9 is composite of 12 Cr, 1 Mo (wt. %), other minor elements such as Ni and C, and Fe as balance.

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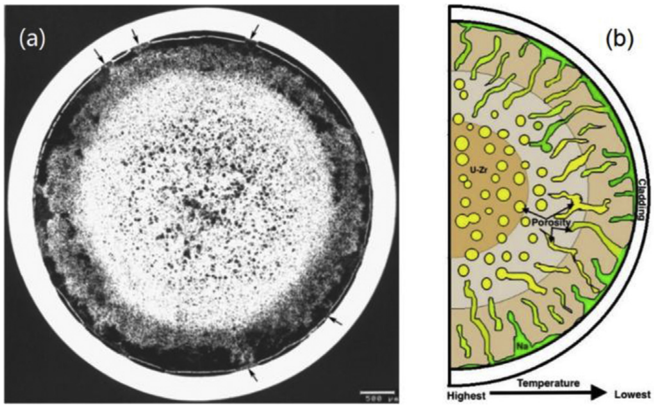

Fig. 1. Transformations of post-irradiation U-Zr fuel. (a) Optical micrograph of fuel cross section (Keiser, 2006), and (b) schematic diagram of half cross section with fuel transformations (Isler, 2017).

portion of fuel pin. The release of fission gas eliminates one of the largest contributors to swelling. The design of smaller smear density has alleviated FCMI and achieved higher burnups.

As allowing the fuel to swell, the transformations associated with higher burnups have become a significant focus. Fig. 1a is an optical micrograph, showing these transformations of the EBR-II irradiated U-23Zr wt. % fuel element T225 with D9[3] cladding at a burnup of 10 at. % (Keiser, 2006). Fig. 1b is a schematic image of an irradiated fuel with several microstructure transformations of interest illustrated, including swelling, porosity, and constituent redistribution. Porosity developing in the swelling fuel is just one of many microstructure evolutions at high burnups. The other microstructure evolution was constituent redistribution in U-Zr fuels during reactor operation. Constituent redistribution results in a relatively higher Zr concentration at the fuel radial center and peripheral regions, while a higher U concentration at the intermediate regions. Previous work has shown that radial temperature gradients generated in rod-type fuel elements appear to be sufficiently large to cause redistribution of fuel constituents (Hofman et al., 1996). The constituent redistribution in U-Zr fuels has some advantages: the increased Zr concentration at the center may improve the solidus temperature of the hottest part of fuel, and the increased Zr concentration at the periphery may increase the chemical compatibility between fuel and cladding. However, the disadvantage of redistribution is also critical as which would result in porosity and void formation in the fuel.

The swelling at the inner hottest region of fuel is dominated by the formation and growth of fission gas bubbles; while at the outer colder region is dominated by the tearing and cavity formation at grain boundaries. In addition to the various swelling mechanisms, the amount of swelling differs as well. The differences of swelling occurring at different regions result in the overall fuel swelling anisotropic and cracks growing at the fuel periphery (Hofman et al., 1990). Caused by the cracks, cavities and fission gas bubbles, the U-Zr fuel may develop a pathway of porosity, which connects from the fuel interior to the fuel-to-clad gap. This interconnected porosity is one of key features in the release of fission gas and the elimination of FCMI. Furthermore, the interconnected porosity is the migration path of lanthanide (Ln) fission products, the chemistry of which plays an important role in fuel-cladding chemical interaction (FCCI) (Kim et al., 2009).

Metallic U-Zr fuels have been used in EBR-II and qualified up to a burnup of 10 at. %, however, such a burnup is still far below the desired burnup of 20 at. % for the advanced sodium-cooled fast reactor (Mariani et al., 2012). A major reason for the limitation of higher burnup is FCCI, which occurs at the fuel/cladding interface during irradiation (Pahl et al., 1993). FCCIs include fuel-cladding interactions (e.g. U-Fe) and lanthanide-cladding interactions (e.g. Ce-Fe). These chemical interactions may lead to cladding wastage with the formation of low temperature eutectics and brittle intermetallics. Low temperature eutectics composite of fuel constituents (U, Pu and Zr) and cladding constituents (Fe and Cr) have been found (Keiser and Petri, 1996; Matthews et al., 2017). Liquefaction and liquid-phase penetration to cladding have been found during irradiation, the liquefied region is coincided with the Fe diffusion depth, the liquefaction threshold temperature is dependent on fuel composition and burnup (Tsai, 1990; Cohen et al., 1993). However, the greatest concern of FCCI is lanthanide-cladding interactions, as lanthanides migrate fast in a fuel and diffuse rapidly into cladding. The present review is focused on the behavior of lanthanides in U-Zr metallic fuels during irradiation, which is different with the previous FCCI reviews (e.g. (Matthews et al., 2017)).

2. Lanthanides at fuel/clad interface

Section 2.1 presents the post-irradiation behavior of lanthanide at the fuel/clad interface. Irradiation may enhance diffusion kinetics, thereby these results are different with the out-of-pile results; however, in-pile tests are limit, it's necessary to understand the chemical interactions of lanthanide and cladding through diffusion couple tests, which is discussed in Section 2.2.

2.1. In-pile data analysis

Both fission yield and fission product decay during the post-irradiation period have an influence on the abundance of lanthanide fission products (Arnold et al., 2015). As indicated by a sample composition of an irradiated U-10Zr fuel pin at around 8 at. % burnup (Mariani et al., 2011), the vast majority compositions of lanthanide fission products are Nd, Ce, Pr and La. Fission products that are relatively insoluble in the U-Zr fuel matrix have been found as precipitates in the pores of fuel, such as Ce precipitates (Pahl et al., 1993) (Itoh et al., 1997) (Pahl et al., 1990). The solubility of Ce in metallic fuel at the typical fuel irradiation temperature (923–973 K) is very low, therefore most of Ce that produced during burning is precipitated. Lanthanides have been experimentally found precipitated in the pores of fuel (Pahl et al., 1990), and they are the major fission products at the outer region of metallic fuels during irradiation (Kim et al., 2014). The temperature gradient in metallic fuel appears to play an important role in the lanthanide migration to the periphery (Keiser, 2006) because the isothermal diffusion couple tests of lanthanide-contained fuel did not show lanthanide migration to the fuel surface (Ogata et al., 1997). Lanthanide precipitates at the fuel periphery have been found even at low burnups, indicating the migration is rapid (Bozzolo et al., 2010).

Post irradiation examination (PIE) data of metallic fuels (U-Zr and U-Pu-Zr) irradiated in EBR-II reactor have been well summarized in the report (Keiser, 2006). The report found that some lanthanides (e.g. Nd, Ce, Pr, La, Sm and Pd) that were originally in the fuel finally were found in the cladding, indicating the occurrence of interdiffusion between lanthanides and cladding when fuel swells. Reports (Keiser, 2006; Mariani et al., 2012) also suggested Nd, Ce, Pr and La as four major lanthanides diffusing into cladding.

The formation of liquid-phase is one of the major type of cladding degradation during FCCI. The liquid phase region coincides with the depth of Fe migration from the cladding as shown from microprobe analysis, the addition of Fe diffusion can form more liquid phase during the test at elevated temperatures (Cohen et al., 1993). Tsai et al. reported that the interdiffusion layers on the fuel and cladding inner surface may liquefy, resulting in liquid-phase penetration into the cladding at a high temperature (Tsai, 1990). Results from the fuel behavior test apparatus (FBTA) on EBR-II fuel pins showed that noticeable liquid phase penetration occurred at temperatures higher than 998 K

[3] Alloy D9 is composite of 15.5 Ni, 13.5 Cr, 2 Mn, 2 Mo (wt. %), other minor elements such as Si and C, and Fe as balance.