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Effects of Rare Earth Elements on the Surface Interaction of U-Zr-Ce Metallic Fuel

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1. Introduction

U-Zr and U-Pu-Zr are well-known compositions for metallic fuel for sodium-cooled fast reactors (SFR). Metallic fuel has many advantages such as simple fabrication procedures, good neutron economy, high thermal conductivity, excellent compatibility with a Na coolant and inherent passive safety[1]. SFR will be developed and constructed by 2028 according to the future nuclear system development plan approved by the Atomic Energy Commission in Dec. 2008. Fabrication technology of metallic fuel for SFR is being developed in Korea as a national nuclear R&D program from 2007[2]. Metallic fuel for SFR should be remotely fabricated under a radiation shielded environment such as a hot cell, because it contains highly radioactive minor actinides (MA) such as Np, Am and Cm. Metallic fuel pins have been remotely fabricated by vacuum injection casting using a quartz mold assembly.

Uranium metal is very reactive with crucible or mold materials such as graphite, quartz and alumina. When there is reaction of melt with crucible or mold, impurity content is increased and composition control becomes difficult. Yttria (Y_2O_3) or zirconia (ZrO_2) slurry coatings are used in metallic fuel casting because they are thermodynamically stable enough to minimize the reaction of uranium melt and crucible or mold materials[3]. However, the effects of refractory coatings on microstructures of the interaction layer on the surface of metallic fuel have not been studied yet. In addition, the effects of the addition of rare earth elements or MA have not fully understood. In this study, the surface interaction layers of U-Zr-Ce metallic fuel were characterized in order to evaluate the effects of rare earth elements on the surface interaction layer formation behavior.

2. Experimental Procedures

Elemental lumps of natural uranium, zirconium and cerium were used to fabricate U, U-10wt%Zr and U-10wt%Zr-(4,6)wt%Ce alloy rods by induction melting. Vacuum injection casting and low pressure gravity casting (Fig. 1) were used to cast long rods with a diameter of 4-10 mm[4]. Graphite crucibles were used and the crucible was coated with Holcote® 110 (zircon based refractory coating). Quartz was used as mold materials. Cast rods were cut into slices and the microstructures and compositions were analyzed by using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

(a) (b)

Fig. 1. Cast rods fabricated by induction melting and low pressure gravity casting; (a) U-10wt%Zr (diameter: 6 mm) (b) U-10wt%-6wt%Ce (diameter: 10 mm).

3. Results and Discussion

A U-10wt%Zr-4wt%Ce rod fabricated by vacuum injection casting using quartz molds without refractory coating as shown in Fig. 2. Cross-section of a fuel rod (Fig. 2a) shows that multi-phase interaction layers of 50 μm were formed at the periphery of the fuel rod. The surface interaction layer at the periphery of a fuel rod was an oxide layer containing Si, Zr, Ce and U. The dark phases in an intermediate layer were Si-Zr compounds. This means that refractory coating of quartz tubes is necessary to retard interaction of uranium alloy melt and quartz tubes. When a rare earth element is added to uranium alloys, the interaction becomes more severe.

(a) (b)

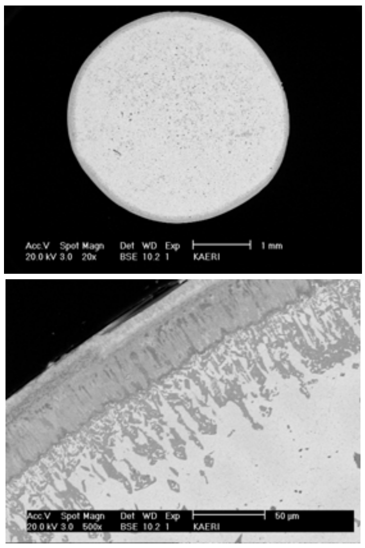
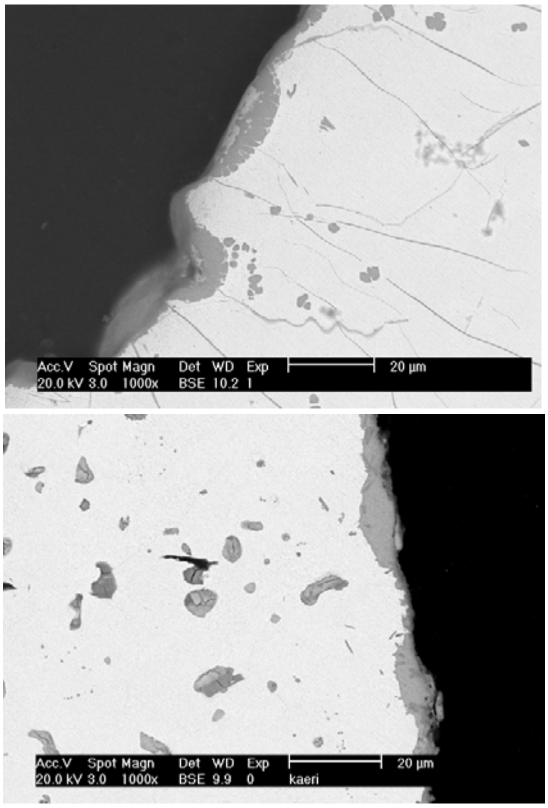


Fig. 2. SEM micrographs of a U-10Zr-4Ce rod fabricated by vacuum injection casting using quartz molds without refractory coating; (a) Cross-section of a fuel rod, (b) surface interaction layer at the periphery of a fuel rod.

Fig. 3 shows SEM micrographs of surface interaction layer at the periphery of U-10Zr rod and U-10Zr-6Ce rod fabricated by low pressure gravity casting using quartz molds coated with HOLCOTE-110. The interaction layer thicknesses were decreased down to 10 μm. The interaction layer of U-10Zr fuel was a Zr-rich phase mainly composed of 95wt% of Zr and 5wt% of U (Fig. 3a). This Zr-rich phase is formed usually when U-Zr alloy is heat-treated in contact with oxygen or nitrogen containing phases. Because Zr has a strong chemical affinity to oxygen and nitrogen, oxygen or nitrogen stabilized Zr-rich phase formed at the surface of U-Zr alloys. Si was not detected at the periphery layer, but ribbon-type $(U,Si)Zr_2$ phases were observed instead. Si may be introduced during melting in a graphite crucible coated with HOLCOTE-110 which contains $ZrSiO_4$.

The interaction layers in U-10wt%Zr-6wt%Ce was different from those in U-10wt%Zr. Ce-rich oxide was mainly observed in the periphery of U-10Zr-6Ce (Fig. 3b). It can be concluded that the addition of rare earth elements in U-Zr alloys enhances the surface oxidation. Whereas the ribbon-type $(U,Si)Zr_2$ phases were not found, Ce precipitates of 5-10 μm were distributed due to limited solubility of Ce in U alloys[5]. Am-rich particles are formed in a similar way after casting of MA bearing metallic fuel since Am also has limited solubility in U alloys.



(a)

(b)

Fig. 3. SEM micrographs of surface interaction layer at the periphery of (a) U-10Zr rod and (b) U-10Zr-6Ce rod fabricated by low pressure gravity casting using quartz molds coated with HOLCOTE-110.

In the future, yttria and zirconia coatings will be applied to crucibles and molds and the resulting surface interaction of fuel rods will be evaluated compared to those fabricated with HOLCOTE-110. Also, the composition of remained refractory coating will be measured in order to manage the radioactive wastes in used crucibles and used molds.

4. Conclusions

Effects of rare earth elements on the surface interaction layer formation behavior were evaluated by characterization of surface interaction layers of U-Zr-Ce metallic fuel. Whereas Zr-rich layers were formed at the periphery of U-Zr fuel rod, Ce-rich oxide layers were observed in U-Zr-Ce fuel rod when refractory coating was applied to quartz molds. Ce addition to U-Zr alloys activate chemical reaction of melt and mold materials. When the refractory coating was not used, silicon containing oxide interaction layers were formed due to the reaction of U-Zr-Ce with SiO_2.

ACKNOWLEDGMENTS

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