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Tailored materials for radioactive waste disposal

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Summary. — This paper reports on the developments for advanced fuel cycles to fully utilize resource materials (*e.g.*, uranium) from used nuclear fuel and decrease the amount and toxicity of waste requiring geological disposal by the U.S. Department of Energy.

1. – Introduction

The U.S. Department of Energy is developing advanced fuel cycles to fully utilize resource materials (*e.g.*, uranium) from used nuclear fuel and decrease the amount and toxicity of waste requiring geological disposal [1]. Electrochemical processing of used nuclear fuel generates chemically distinct metallic and salt-based waste streams [2]. Aqueous processes generate high-level radioactive gaseous and oxide waste streams that must be immobilized for disposal. Advanced multiphase materials are being used to immobilize various individual and combined radiological wastes in durable alloy, ceramic, glass-ceramic, and metal-oxide cermet waste forms. These waste forms can be tailored for waste stream compositions, key radionuclides, processing methods, existing regulations, and durability under anticipated storage and disposal conditions.

Key aspects of waste form development include (1) the capacity to accommodate waste constituents in durable host phases at acceptable loadings, (2) reliable production methods that generate waste form products having consistent properties and predictable behavior, and (3) confidence that the waste forms will meet regulatory requirements during handling, storage, transport, and permanent disposal. Waste form development at Argonne includes understanding how processing variables affect radionuclide immobilization and waste form performance and determining process control limits that can be used to ensure consistent chemical, physical, and radiological properties during waste form production, including waste loading. In addition, insights from determining radionuclide release modes, understanding the degradation mechanism of the waste form matrix and host phases, and quantifying the effects of environmental variables on the

degradation kinetics are used to develop quantitative models of waste form behavior in disposal facilities over the regulated service life.

In the U.S., regulations require demonstration that a disposal system will meet limits established for individual protection, human intrusion, and protection of groundwater within reasonable expectations based on technical safety analyses and performance assessment (PA) of the facility including engineered and natural barriers. Waste forms provide the first of several transport barriers utilized in repository designs to ensure regulatory compliance. A mechanistic understanding of waste form degradation processes and environmental effects provides confidence in the predicted long-term performance of the waste form. In many cases, the durability of the host phase is used to calculate the release of a radionuclide and the source term for contaminant transport models is calculated as the product of the radionuclide inventory and waste form degradation rate.

Waste forms are used to contain radioactive wastes during handling, storage, transport, and long-term disposal, but the primary performance measure is mitigating the release of radionuclides after they are disposed in an engineered geological facility. The ability to reliably predict waste form corrosion rates that provide radionuclide source terms used to assess the long-term performance of a disposal facility under evolving environmental conditions is an important aspect of waste form development. These include intrinsic characteristics and performance measures that are used to determine if a particular waste form is acceptable for disposal.

An iterative process is followed at Argonne to develop durable waste forms and mechanistically-based degradation models that are used to optimize both formulations and performance. An appropriate matrix material is selected so that radionuclides are immobilized in durable host phases. Multiphase materials can include host phases tailored for particular constituents in a waste stream, including glass/glass, glass/ceramic, metal/metal, and metal/ceramic composites. Material-specific testing is used to develop a mechanistic understanding of host phase corrosion behavior and interactions to develop source term models that capture dependencies on key waste form characteristics and disposal environment variables [5]. The goal is to develop a characteristics-based approach for demonstrating product acceptability.

2. – Material and methods

Waste form materials, test methods, and material-specific degradation models have been developed at Argonne for metallic, oxide, combined metal/oxide, and salt waste streams, including challenging waste streams dominated by plutonium or technetium, and directly-disposed UO2-based spent fuel. Table 1 summarizes alternative waste forms evaluated for use with different waste streams and fig. 1 includes scanning electron photomicrographs showing the complex microstructures of several multiphase waste forms. Waste form development includes the examination of material microstructures to measure the dispositions of radionuclides in different host phases and interfaces between phases to assess the effectiveness of processing. Trim reagents can be added to improve the durabilities of specific phases and cohesiveness.

A primary challenge to qualifying waste forms for disposal is predicting long-term degradation behaviors in evolving repository environments to provide confidence that regulatory requirements will be met. Test methods that are sensitive to specific reaction processes are used to understand and the waste form corrosion behavior and quantify dependencies on environmental variables, measure the kinetics of key processes and accelerate corrosion to simulate aspects of long-term degradation [3]. For example, the

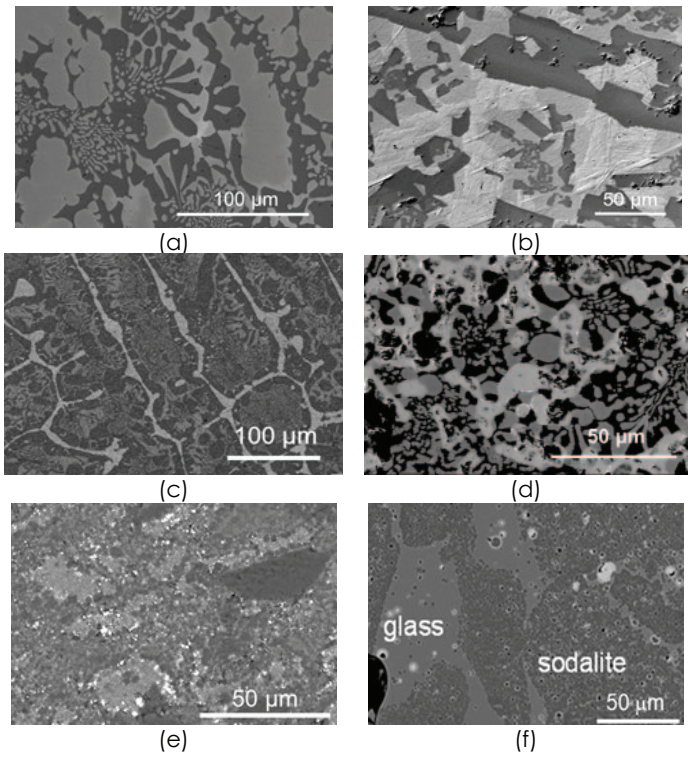

Fig. 1. – Image of non-destructive evaluation of high-energy X-ray computed tomography.

corrosion behaviors of metallic phases will be sensitive to the redox strength (solution Eh), pH, and chloride contents of seepage waters filling breached waste packages. The electrochemical effects of the groundwater on the waste form oxidation reactions can be studied efficiently and analytically quantified by using electrochemical techniques.

TABLE I. – *Waste streams and alternative waste forms.*

Waste Stream	Waste Forms
Cladding hulls and metallic fuel waste	Multiphase Fe-Zr alloy
	Multiphase Zr-Cr alloy
	Glass-bonded sodalite ceramic waste form
	Silica-alumina-phosphate (SAP) glass
Chloride salt waste	Iron phosphate glass-ceramic
	Tellurite glass
	Borosilicate glass
Oxide waste	Lanthanide borosilicate (LABS) glass
	Alloy-ceramic cermet
Iodide waste	AgI-bearing composite materials
	Ag-bearing Te-Bi glass
Technetium	Steel alloy
Plutonium oxide	Lanthanide borosilicate (LABS) glass

Electrochemical test protocols in the Argonne ElectroCorrosion ToolkitTM are used to relate corrosion behavior to phase composition and environmental conditions, including the effects of passivation and galvanic couples [4]. Those methods combine metallurgical, electrochemical, and microscopic techniques to identify the material and environmental variables affecting the degradation rates and quantify dependencies on the waste form composition and environmental variables.

Various immersion test methods (*e.g.*, ASTM 1220, ASTM 1285, ASTM 1663) are used to impose different solid/fluid interaction conditions to gain insights into the degradation mechanisms of glass, mineral, and ceramic-based waste form materials. These include different test conditions that maintain far-from-saturation dilute conditions or promote saturated conditions, use static of flowing conditions, and test conditions that accelerate particular processes or the overall reaction progress. The relevance of test responses to material performance are assessed based on the degradation mechanism and anticipated disposal conditions. Depending on the waste form material, assessments can combine electrochemical and immersion test methods with metallurgy, microscopy, and solution analyses to understand corrosion mechanisms and quantify the effects of waste form composition and solution properties. Results of appropriate tests provide a mechanistic basis to correlate phase compositions and environmental conditions to corrosion behavior, which leads to improved formulations, enhanced production controls, and reliable long-term performance models for specific storage and disposal environments. Representative results of combined metallography, electrochemical measurements, and microscopy used to assess the chemical durabilities of metallic and cermet waste form materials are provided as examples.

3. – Metallic waste forms

Stainless steel-based metallic waste forms (MWF) were developed at Argonne in the 1990s to immobilize high-level radioactive wastes from the electrometallurgical treatment of used sodium-bonded nuclear fuel [5]. These MWFs are produced by alloying residual metallic fuel wastes and steel cladding hulls recovered from the electrorefiner with small amounts of trim metal additions (*e.g.*, Zr, Cr, and Mo) to produce a multiphase alloy composed of physically, chemically, and radiologically durable intermetallic and solid solution phases that contain the radionuclides. Waste forms can be produced by directly melting wastes at temperatures near 1650 °C because waste constituents having high melting temperatures dissolve into the molten steel. Other MWFs are being developed to immobilize waste streams anticipated to be generated from advanced fuels in HT9 steel cladding and oxide fuel in Zircaloy cladding [6,7]. The formulations of MWFs are tailored to provide corrosion-resistance host phases to retain radionuclides during production and disposal that can be generated reproducibly at practicable processing temperatures. This includes adding trim metals and combining wastes to provide low-temperature eutectics for processing, consolidation of phases (wetting), and passivating additives for corrosion resistance.

Figure 2(a) is a low magnification Scanning electron microscopy (SEM) image of a steel-zirconium-based metal waste form composed of two major phases [6]. The lighter grey phase is a $ZrFe_2$ intermetallic phase and the darker grey phase is a ferrite phase. The energy dispersive X-ray (EDS) spot analyses show that uranium is immobilized in the ZrFe2 intermetallic phase and technetium is immobilized in the ferrite phase. Figure 2(b) shows potentiodynamic (PD) scans of polished multiphase MWFs that show the beneficial effects of added trim metals and metallic fuel waste elements on corrosion

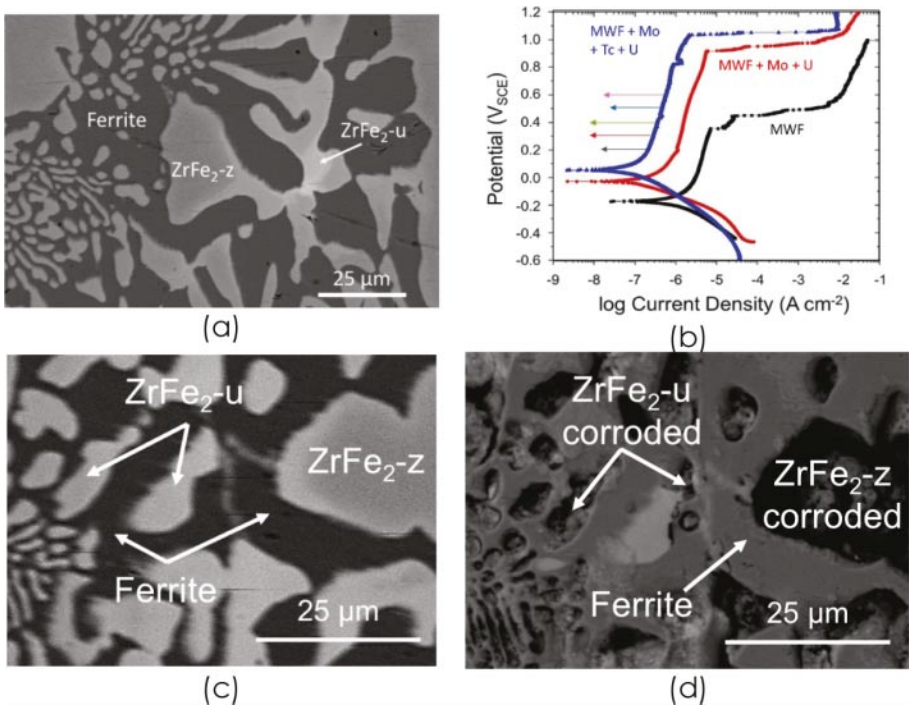

Fig. 2. – Image of automatic sorting technology combining sensing and information processing technologies.

resistance spanning the range of possible solution redox conditions. Added trim metals enhance durability by forming stable passivation films, which have been shown to decrease the corrosion current by a factor of 100x under oxidizing conditions (as indicated by the arrows in fig. 2(b)). Passivation-based degradation models have been developed for MWFs with terms for dependencies on solution pH, redox, chloride content, and temperature. Figures 2(c) and (d) are high magnification SEM images of a region in the MWF+Mo+Tc+U material before and after the PD scan. Comparison of the images in figs. 2(c) and (d) shows $FeZr_2$ intermetallic phases are preferentially corroded at a high voltages during the PD scan. The currents measured in follow-on tests at fixed potentials (indicated by the arrows in fig. 2(b)) are used to track surface passivation and corrosion rates by using Faraday's law.

4. – Cermet waste forms

Metal waste forms can accommodate small amounts of oxide wastes such as residual oxides remaining in the metallic fuel wastes and added oxides [8]. Photomicrographs of a cermet made with HT9 cladding, trim metals, and surrogate oxide waste are shown in fig. 3. The added oxides were either reduced and alloyed or converted to insoluble actinide and lanthanide-bearing zirconates during processing at 1600 °C for three hours. The sintered ceramic phases form a porous lattice that is filled with metal. The product forms as a core of mixed alloy and oxide composite with small regions of extruded metal. Figure 3(a) is a SEM image of the metallic part that is composed of ferrite and $(ZrMo)Fe_3$

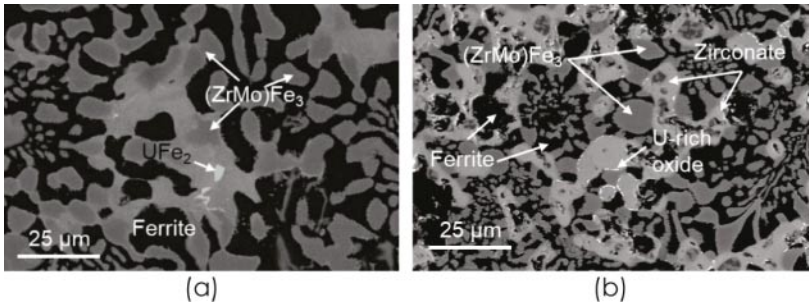

Fig. 3. – SEM analyses show microstructures of (a) metallic and (b) composite parts of HT9-based cermet waste form.

intermetallic phase with a small amount of an UFe $_2$2 intermetallic. Figure 3(b) is an SEM image of the cermet core that consists of sintered ceramic phases and the same metallic phases that form the metallic part. Several regions of unreacted U-rich oxide that remain at interfaces between zirconate and intermetallics indicate the conversion process.

Figure 4 shows SEM images of a cermet made with 316L stainless steel cladding, trim metals, and ZrO_2 as a surrogate for oxide waste by heating at 1650 °C for three hours [9]. Figures 4(a) and (b) are high magnification SEM images of the same region in the cermet before and after a PD scan in pH 10 buffer at room temperature. The SEM image in fig. 4(b) shows regions of $FeZr_2$ intermetallic phases were preferentially corroded at a high voltages relative to the ferrite and ZrO_2 phases. This indicates the $FeZr_2$ intermetallic phases is not an effective host phase.

5. – Conclusion

Our approach to developing durable waste forms considers the compatibility of waste streams with the host matrix, the retention of radionuclides during processing, sequestering of radionuclides in durable host phases, nuclear accountancy, and demonstrating compliance with regulatory criteria. The suitability of alloy, ceramic, cermet, glass, or glass-ceramic host matrix for a particular waste stream is assessed based on processabil-

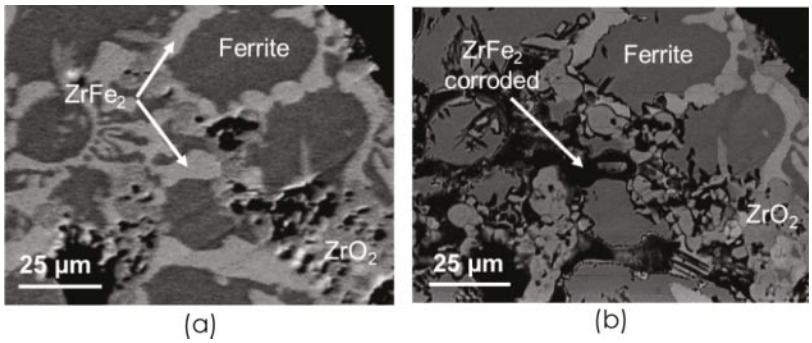

Fig. 4. – Microstructure of 316 stainless steel-based cermet (a) before and (b) after PD scan.

ity, waste loading capacity, and flexibility, the effectiveness of process controls, and predicted long-term degradation resistance in disposal environments based on mechanistic understanding of key degradation processes. Different processes control the durabilities of different waste form materials. The chemical durability and degradation behavior of waste form materials are measured using tests selected based on mechanisms of host phase degradation and modes of radionuclide release. Several test methods are typically used to highlight processes that dominate under different conditions. Consensus standard test methods are used when appropriate, and new methods are developed when needed to understand and quantify particular processes. For example, the Argonne ElectroCorrosion ToolkitTM was developed to assess materials with phases that degrade by electrochemical processes including metallic waste forms and directly disposed commercial UO_2 fuel. Other methods have been developed for affinity-controlled degradation mechanisms of glass and ceramic-based waste forms.

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