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PRODUCTION OF METAL WASTE FORMS FROM SPENT FUEL TREATMENT

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ABSTRACT

Treatment of spent nuclear fuel at Argonne National Laboratory consists of a pyroprocessing scheme in which the development of suitable waste forms is being advanced. Of the two waste forms being proposed, metal and mineral, the production of the metal waste form utilizes induction melting to stabilize the waste product. Alloying of metallic nuclear materials by induction melting has long been an Argonne strength and thus, the transition to metallic waste processing seems compatible. A test program is being initiated to coalesce the production of the metal waste forms with current induction melting capabilities.

I. INTRODUCTION

As operation of the Experimental Breeder Reactor II (EBR-II) ceases, the need to condition its spent nuclear fuel for disposal in a geological repository emerges.[1] Characteristic to the EBR-II spent fuel is the chemically reactive bond sodium which was essential for the transfer of heat from the fuel to the primary reactor coolant. Treatment of the spent fuel to remove the metallic sodium would assure its chemical stability prior to disposal. The proposed method of treatment for EBR-II spent fuel is a pyrometallurgical process that utilizes techniques originally intended for the Integral Fast Reactor (IFR) fuel cycle. One of the most salient elements of the technology is the minimization of waste by production of qualified waste forms. In addition to EBR-II fuel, there are several other types of spent nuclear fuel within the DOE complex that are currently not acceptable for direct disposal because of their chemical or nuclear activity. Incorporation of these other types into the Argonne National Laboratory (ANL) conditioning program is being considered.

Pyroprocessing of spent EBR-II fuel at ANL consists of two high temperature processes: electrorefining and cathode processing.[2] Preparation of the spent fuel for electrorefining is performed by shearing the sodium bonded clad fuel into 6.4 mm (0.25 inch) segments. The segments are then loaded into the electrorefiner for dissolution of the fuel and sodium into a molten LiCl-KCl electrolyte at 500°C. Electrotransport of the actinide species from the fission products yields both a solid and liquid cathode product. The solid cathode is typically uranium while the liquid cathode is plutonium and uranium. Distillation of the process fluids, LiCl-KCl salt and cadmium, is performed at the cathode processor to consolidate the actinide ingot.

Following operation of the electrorefiner, the unreacted cladding hulls, along with insoluble noble metal fission products, are stabilized into a metal waste form.[3] The insoluble noble metals are removed from the electrorefiner by pumping the salt and cadmium through a sintered steel filter while the cladding hulls, loaded into baskets prior to electrorefiner operation, are simply dumped from the baskets. Minor amounts of actinides may also be included in the metal waste form due to the adherence of salt to the cladding hulls following electrorefiner operation.

DISCLAIMER

The reference metal waste form, currently being investigated at Argonne-East, is an iron-based zirconium alloy. Small-scale tests have been conducted to date to determine phase distributions and corrosion resistance of various iron-zirconium alloys. Engineering scale tests are planned at Argonne-East using an induction furnace in anticipation of final demonstration at Argonne-West. Three induction furnaces, detailed in Section II, are available at Argonne-West for metal waste form development. Their original purpose was for casting metallic fuel in support of EBR-II operations.

Induction melting was selected for fuel fabrication at ANL based on its high thermal efficiencies resulting in superior alloying capabilities, thus making it one of the most effective means of melting metals. Within the nuclear industry, the development of processing techniques for radioactive waste materials has led to the advent of induction melting technologies.[4] To date, the two most common applications of induction melting to nuclear waste processing involve cladding hulls and contaminated scrap.

Following the separation of spent nuclear fuel from clad tubing, cladding hulls are consolidated by induction melting to achieve fixation of the radionuclides into a suitable containment matrix. Both zircaloy and stainless steel cladding hulls have been stabilized into homogeneous metal ingots.[5-9] The most significant benefits from the process are the concentration of residual actinides into a secondary waste form and a significant reduction in surface area/volume.

Affirmation of these characteristics has also been demonstrated during the densification of slightly contaminated metallic scrap by induction melting.[10-15] The immobilization of surface contamination into a metal matrix as well as volume reduction are the most notable attributes from the process. One particular observation worth noting is the partitioning of Cr and Ni into chemically stable Fe-rich crystalline phases.[10] Hence, the leachability of Cr, a listed hazardous waste and minor constituent of stainless steel, may not be of consequence for the ANL metal waste form.

II. EQUIPMENT

A. Early History

Early planning for the EBR-II reactor fuel determined that it was necessary to develop a simple fuel fabrication process because, following the initial core loading, the process would be a remote operation on irradiated fuel discharged from the reactor. EBR-II and the Fuel Cycle Facility (FCF) were initially designed and operated as an integrated reactor-reprocessing facility.

The primary step in the fuel fabrication consisted of using the pressure of argon gas to fill evacuated molds. This basic fuel fabrication technique was used in both the cold prototype and hot production line and the subsequent coldline production operations.

In 1969, the missions of EBR-II and FCF were changed. FCF was redirected to the development of remote handling equipment and examination of irradiated nuclear fuels and materials. Since that time, the EBR-II driver fuel has been made from unirradiated material in cold production lines.

B. Experimental Fuels Laboratory (EFL)

The EFL was initially created for the purpose of demonstrating the capability of casting prototypical fuel that would be used in the IFR program. The entire operation, which consists of casting, processing, and loading of the fuel into element jackets, is housed within a structure of two plutonium qualified glove boxes connected end-to-end.

The EFL is located in a room 4 m by 8 m and contains all the casting equipment with the exception of the glove box ventilation and purification systems which are housed in the basement. Two glove boxes measuring 1 m by 2 m by 1.5 m high are connected end-to-end and house all those components required for casting and encapsulating the fuel slugs. The major components within the glove boxes are the casting furnace, shearing and measuring equipment, balance, settling furnace, and holding racks. Two small chain hoists are also enclosed in the glove boxes. Additional information about the EFL furnace is given in Table 1.

C. Fuel Manufacturing Facility (FMF)

The FMF was built on the lessons learned from the FCF, coldline production, and the EFL induction furnaces. Maximum use of modular design concepts was implemented to minimize installation and maintenance efforts and to prototype designs intended for remote, in-cell applications for the future IFR demonstration program.

The furnace is located in a controlled ventilation air atmosphere room and composed of a 61 cm diameter by 122 cm long pressure/vacuum vessel. Two 25 cm nozzle penetrations on top of the vessel allow installation of mold actuator assemblies which are used during casting operations to lower the molds into the crucibles for injection casting. The coils, bus bars, and crucibles are supported on a carriage which is attached to the access hatch. The coils and crucibles can be withdrawn from the furnace by axially retracting the access hatch and the attached carriage from the shell. The hatch and carriage assemblies are withdrawn into a ventilated shroud to assure containment and control of contamination.

The vacuum and pressurization system, associated valves, gauges, and 25 kW solid state power supply are located in adjacent rooms to the furnace. Further data regarding the FMF furnace is shown in Table 1.

D. Fuel Cycle Facility (FCF)

Following the refurbishment of the FCF for the IFR demonstration program, an induction furnace was positioned in the argon cell for fuel fabrication. The furnace vessel is composed of two sections, a 71 cm diameter by 61 cm long section and a 25 cm diameter by 53 cm long section. The top 25 cm flange and bottom 71 cm flange are remotely operated clamped flanges. The top flange allows access into the top of the furnace for loading of the crucible and mold pallet for injection casting. The bottom flange allows the vessel to be removed for access to the furnace internals.

The vacuum and pressurization system is located adjacent to the furnace in-cell. The power supply leads run from the furnace out of cell and to the 30 kW power supply in the basement of FCF. The casting furnace system and process are controlled and monitored with a

Table 1. Induction Furnace Capabilities

	EFL	FMF	FCF
Maximum Temperature (°C)	1700	1700	1700
Minimum Pressure (mm Hg)	0.2	< 1	< 1
Maximum Pressure (mm Hg gauge)	1551	1810	5171
Crucible Dimensions (cm): OD ID Height	6.4 5.7 12.7	17:1 15.6 22.9	23.8 21.9 19.1
Power Supply			
Output Power (kW) Voltage (V) Current (A) Frequency (kHz)	7.5 220 300 10	25 400 650 3 to 10	30 400 720 2.5 to 3
Coil			
Number Material Turns Dimensions (cm): ID Height	1 Solid OFHC Copper 10 10.2 19.7	2 Solid OFHC Copper 12 21.0 23.6	1 Solid OFHC Copper 11 30.5 22.2
Mechanical Stirrer	Yes	No	No
Tilt Pour Mechanism	Yes	No	No

programmable logic controller (PLC) with inputs from the associated instrument set which includes thermocouples (Types C and K), pressure and vacuum sensors, limit switches, and input from the induction power supply. The system can be operated in three different modes: manual, semi-automatic, and automatic. All control parameters can be changed for each casting run. Furnace details are given in Table 1.

III. TEST PROGRAM

A. Crucible Compatibility Tests

In order to produce a stable, homogeneous metal waste form, it is imperative to identify crucible materials that do not interact with the melt. Since the crucible needs to be reusable, the waste form must be easily removed from the crucible; the crucible should not display any residual material attached to its surface after a casting; and, the crucible must exhibit good thermal-shock resistance, since no cracks can be tolerated during the heating or cool down procedures. Any interaction between the melt and the crucible would result in the development of phase layers at the melt-crucible interface or in a reduction process where elements in the melt, like Zr, reduce the crucible material. Reduction of the crucible can result in the transport of impurities like C, O, or N into the melt. Initial studies have shown that discrete stabilized Zr globs can form in the melt if there is a steady supply of impurities from the crucible.[16-17] These globs are unfavorable in the context of developing stable metal waste forms. The presence of discrete Zr-rich globular phases in the final ingot limits the homogeneity of the material which may adversely affect the mechanical and corrosion properties of the final metal waste form.

The crucible-melt compatibility tests to be conducted will involve casting metal waste forms utilizing a variety of crucible materials, and then analyzing the ingots (and the crucible in the cases where melt-crucible interaction occurred) using scanning electron microscopy with energy dispersive spectroscopy and optical microscopy. These analyses will be utilized to determine the microstructure of the castings, the amount of melt-crucible interaction, and the compositions of the phases observed in the ingot microstructures. The choice of crucibles will be based on choosing the most thermodynamically stable, thermal-shock resistant, and wetting resistant materials that can be employed to cast stainless steel, Zr, and noble metals. Initial studies have isolated yttria as a possible once-through crucible for casting stainless steel-Zr materials.[3] There is limited melt-crucible interaction, but yttria is useful for a one time casting in order to investigate microstructures and other properties of the ingots.

Stainless steel with 15 wt.% Zr will be the first alloy cast. Nascent waste form studies have shown that materials with this composition are homogenous, corrosion resistant, and melt at relatively lower temperatures due to the alloy's proximity to the eutectic composition on the Fe-Zr phase diagram.[3] The first studies will be conducted using 316 stainless steel based materials, since this steel makes up the bulk of the material to be processed. Subsequently, D9, 304, and HT9 stainless steel based materials will be cast. The most notable difference between the stainless steels to be processed is that HT9 exhibits a martensitic microstructure, while D9, 304, and 316 are austenitic stainless steels. Additionally, D9, 304, and 316 contain at least 10 wt.% Ni, and HT9 comprises only 0.5 wt.% Ni. Previous casting experience with HT9-based materials has shown that when 15 wt.% Zr is added, the microstructure of the material consists of a high Fe matrix phase with Fe-Zr precipitates.[3] Similar structures are expected to develop for austenitic stainless steel based materials.

Next, melt-crucible compatibility tests will utilize stainless steel-15 wt.% Zr materials with additions of noble metals. The noble metal fission products, which are noble relative to our process, constitute about 1.5 wt.% of an irradiated fuel rod, and they include, in order of decreasing concentration, Ru, Pd, Ag, Cd, Rh, Tc, Sb, and Sn. The other noble metals (Fe, Cr, Ni, Mo, Mn, Ti, and Co) are actually activation products of the stainless steel. Most compatibility tests utilizing noble metal containing materials will involve casting alloys comprised of stainless steel and the major noble metal elements, viz. Zr, Pd, Rh, and Ag. Particular attention will be given to the effects that the addition of individual constituents have on melt-crucible compatibility. Ultimately, the casting studies will investigate the effects of adding 1-2 wt.% U and 1-2 wt.% Pu to the melts. Plutonium and uranium loadings may have an application in waste disposal forms or weapons plutonium disposition. Further, it is of general interest to note the particular phases in the metal waste form microstructure in which U and Pu are soluble. Casting studies for U and Pu containing materials will be performed in FCF.

Peripherally, the effects of varying the casting process parameters may be investigated to see how metal waste form production can be optimized in the context of

limiting melt-crucible interactions. The parameters may include stirring rates, cooling rates, heating rates, the use of fluxing agents and mold washes, and compositional variations of the cast alloys.

B. Modifications to FMF Furnace

The FMF casting furnace was set up for development work in injection casting of uranium-base alloys, and will require some modification before use with stainless steel alloys. The particular problems of concern are the solubility of carbon from the crucible in the iron-based melt, and limitations on the pallet motions and mass limits for the existing pallet drive system.

The furnace was designed with a suscepting graphite crucible because the relatively small and highly variable batch sizes, would be difficult to inductively couple directly. The same is true for the proposed stainless steel alloy tests, so the suscepting crucible will be kept and a ceramic liner crucible will be added to eliminate the iron/carbon solubility problem. The induction heating power supply is adjustable in frequency from 3 to 10 kHz, so it should be possible to maintain electromagnetic stirring of the melt in the new configuration.

The existing pallet drive system is pneumatically driven and does not allow simple adjustment of either stroke length or speed. Currently planned testing requires only simple glass mold injection casting of sample pins, which should be achievable with the existing hardware. Any future testing of injection cast or bottom pour ingots may require substitution of an electrical pallet drive system like the one on the FCF furnace. Argon gas is used both to power the FMF pneumatic drive for the pallet and to provide cooling gas in the pallet region to aid controlled rapid solidification of the presently-cast uranium alloy fuel pins. It should be capable within its present adjustment range of providing sample and ingot cooling for the stainless steel alloy tests.

IV. FURTHER INVESTIGATIONS

A. Radionuclide Distribution

As elements of the test program are implemented in the FCF furnace, an area of particular interest is the behavior of radionuclides during the melting process. Determination of their distribution into the ingot, slag, and off-gas will be of significant relevance to final stability testing on the metal waste form. The transfer of radionuclides from the melt to the slag and off-gas would enhance the immobilization properties of the ingot, albeit at the expense of another waste form, the slag. Formation of a slag with fluxing agents could be used for the extraction of actinide contaminants.

Previous studies regarding the melting of radioactive iron-based materials have revealed that the α-emitters (^{235}U, ^{238}U, ^{241}Pu, and ^{244}Am) as well as ^{90}Sr concentrate in the slag while ^{137}Cs is volatized and retorts to the off-gas.[7-10] Displacement of these nuclides can be attributed to their relative oxidation state for the slag and their volatility for the off-gas when compared to the other nuclide species present. In all cases, the structural-related radionuclides (^{60}Co and ^{54}Mn) remained in the ingot.

B. Modifications to FCF Furnace

Production casting of metal waste forms in the FCF furnace should allow the use of larger and less variable batch sizes. This allows consideration of more commercially prototypic operations, such as direct inductive coupling to the charge material instead of a graphite crucible, and use of bottom-pour or tilt-pour furnace designs to produce large chill-cast ingots.

The current graphite crucible could be replaced with a ceramic crucible with all of the power supply output going directly into the charge. This would permit more rapid heatup of the charge and quick, more vigorous electromagnetic stirring of the melt. This in turn would lead to less heating of the furnace materials during the run, faster furnace cooldown, and much quicker furnace cycle times. Refractory metal crucibles that did not require recoating every run would also produce most of these benefits.

The existing injection casting technique can provide a wide variety of ingot forms, but in general will have slower cooling rates as the individual ingot mass goes up. This will lead to coarser microstructure, and perhaps increased segregation and degraded corrosion performance. Larger ingots could be chill cast into graphite or copper molds if the furnace design were converted to a bottom-pour or tilt-pour design. The necessity for these modifications will be evaluated during the early test phases.

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Westphal 99 6

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