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Zirconium determination by cooling curve analysis during the pyroprocessing of used nuclear fuel

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ABSTRACT

An alternative method to sampling and chemical analyses has been developed to monitor the concentration of zirconium in real-time during the casting of uranium products from the pyroprocessing of used nuclear fuel. The method utilizes the solidification characteristics of the uranium products to determine zirconium levels based on standard cooling curve analyses and established binary phase diagram data. Numerous uranium products have been analyzed for their zirconium content and compared against measured zirconium data. From this data, the following equation was derived for the zirconium content of uranium products:

$$Zr = 0.14M + 131.56 - 12.63(348.65 - 0.16LT)^{1/2}$$

where M is the mass (kg) of the ingot and LT is the liquidus temperature (K) found by cooling curve analyses. Based on this equation, a reasonable fit of calculated to measured zirconium content was established considering the errors in the system.

1. Introduction

During the pyrometallurgical treatment of used Experimental Breeder Reactor-II (EBR-II) fuels, a casting step was incorporated to originally cast metal fuel into elemental form for continued irradiation of the fuel in a fast reactor [1,2]. More recently, the casting step has been utilized for down-blending of uranium products to low enriched uranium (LEU) and sampling purposes [3]. Sampling of the uranium products involves injecting molten metal into quartz molds and solidifying the metal so that representative samples can be sectioned and analyzed by dissolution chemistry. Since the uranium products are slightly radioactive [4], the casting and chemical analyses are performed in shielded facilities with remote handling capabilities.

A viable alternative to the labor intensive sampling and analysis program is to monitor the melt in real-time for impurity content by cooling curve analysis (CCA) which is common practice in the steel industry [5]. Since phase equilibria have been established for countless systems, monitoring the cooling curve of a simple binary system is straightforward in that correlation with a liquidus curve is feasible. For the uranium products from the pyroprocess, the impurity with the greatest concentration is zirconium. Zirconium derives from the original fuel as an alloying agent with uranium and can be carried along electrochemically due to its similarity with uranium [6,7]. Thus, the zirconium content of the uranium products can be determined by analyzing the casting cooling curves and comparing against the U–Zr phase diagram for compositional data.

The purpose of this paper is to describe the casting equipment and operation using representative cooling curve data such that the zirconium content of the uranium products can be determined. The zirconium content found by conventional chemical analyses will be contrasted against that found from cooling curve analysis. Due to the inherent characteristics of the casting system, an offset exists between the measured and calculated zirconium levels. This offset will be addressed and quantified. Also, a brief discussion on the liquidus portion of the U–Zr phase diagram will also be included to establish a basis for liquidus temperatures.

2. Experimental

The development of metallic fuel casting by injection into quartz molds was initiated for the original EBR-II fuel cycle in the 1960s [2,8]. Based on the success of this method and the integrity of the fuel for reactor operations, several different casting furnaces have been utilized for the production of metallic fuel for EBR-II including the current unit producing uranium products from the pyroprocess. The current unit is located in a hot cell environment where all operations are performed remotely with electro-mechanical

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manipulators. More than 100 heats of the current casting furnace have been performed to down-blend, sample, and produce uranium products ranging in size from 15 to 50 kg. The uranium products, following characterization by chemical analyses, are placed in interim storage awaiting final disposition.

Shown in Fig. 1 is a schematic of the inductively-heated casting furnace utilized for the melting and casting of uranium products. The furnace is capable of temperatures as high as 1873 K and vacuum to less than 1333 Pa (10 Torr). The vacuum capability is instrumental in casting molten metal into the quartz molds. Following a system evacuation, the molds are submerged into the melt and the system is repressurized rapidly to fill the molds. A graphite crucible coated with yttria contains the melt and two thermocouples (type C), located under the crucible, to monitor the crucible temperature during the casting process. The temperature measurements from the thermocouples are recorded by a data archival system. An immersion thermocouple was also designed into the equipment to monitor the temperature of the molten alloy during the casting process but has only been used sporadically. Although feasible, its use for cooling curve analysis would require either consumable components or reheat of the solidified ingot for hardware removal.

A typical operation of the casting furnace includes loading the crucible with a previously consolidated ingot from cathode processing, heating the furnace above the melting point of the alloy (superheat), casting the molten alloy, removing the quartz molds from the melt, and allowing the furnace to cool passively. Superheat is required to compensate for heat losses incurred during the submersion of the molds into the melt and assures a molten mass is available for casting. Water cooling of the casting furnace is not an option due to criticality concerns in the argon atmosphere of the shielded hot cell. Following a casting, the cast pins are removed from the quartz molds, sectioned, and sent to the analytical laboratory for chemical analyses. In the laboratory, the sections are dissolved in nitric acid and analyzed by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) techniques. A Prodigy (Teledyne Leeman Labs, Hudson, NY) instrument was utilized for ICP-AES. The ICP-AES has been modified for use with radioactive samples to limit personnel exposure by operation of the plasma in a shielded glovebox and monitoring of the transmission by a spectrometer located exterior to the box.

2.1. Cooling curve analyses

Depicted in Fig. 2 is a typical time–temperature plot for the casting operation as taken from the thermocouples located underneath the crucible. The mass of this uranium product was 18.2 kg and the measured zirconium content was 0.39 mol%. Fluctuations in the maximum temperature are induced by cycling of the power input to the furnace to assure stirring of the molten metal. Inflections are visible on the cooling portion of the plot indicating phase changes. Point 1 represents the liquidus temperature of the alloy and points 2 and 3 represent allotropic phase transitions of uranium. The inflections are due to the evolution of latent heat during the phase transitions causing the normal cooling rate of the alloy to be affected. It is interesting to note that the inflections are clearly evident despite the use of thermocouples external to the crucible.

The exact point of inflection on a cooling curve is determined by taking a first derivative of the time–temperature data [5]. For the data provided in Fig. 2, a plot of the first derivative (dT/dt) versus temperature is shown in Fig. 3. Point A on Fig. 3 depicts the first inflection (point 1 on Fig. 2) on the cooling curve at approximately 1473 K and represents the liquidus temperature of the melt.

Traditional cooling curve analyses are performed utilizing internal measurements taken either in the center of the melt or at the wall in order to observe the solidification characteristics. It is also for this reason that thermal analyses using calorimetry are performed with thermocouples in contact with the molten material of interest. Induced by these measurements is a discrepancy from the true equilibrium or liquidus temperature caused by the cooling rate of the melt [5,9]. The discrepancies are small for calorimetry considering the sample sizes but may be significant for larger masses. Thus, although in situ temperature measurements are the accepted practice, it should be realized that their measurements have limitations, particularly for larger systems.

Since solidification of the metal occurs from the exterior of the melt to the center, thermocouples located near the wall, both interior and exterior to the melt, record data during solidification that are comparable but differ by the thermal characteristics of the crucible. By balancing heat transfer between a molten metal and a mold, Chvorinov derived a rule that correlates solidification

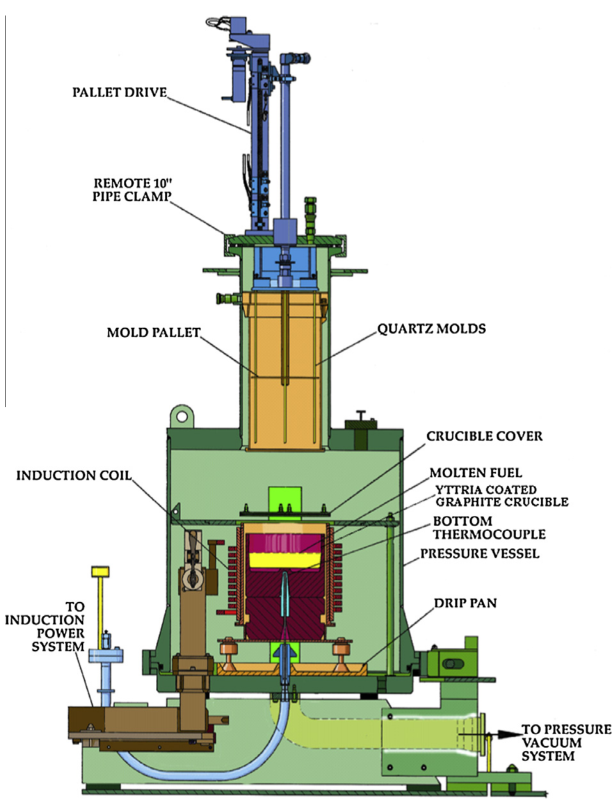

Fig. 1. Schematic of casting furnace.

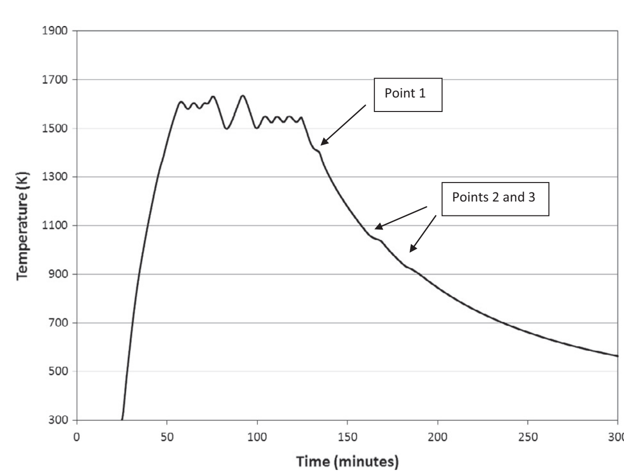

Fig. 2. Typical heating and cooling curve for uranium product casting operations.