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Thermophysical investigations of the uranium–zirconium alloy system

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ABSTRACT

The solid phase transformation behavior of uranium–zirconium (U–Zr) alloys (U–0.1, 2, 5, 10, 20, 30, 40, and 50 wt% Zr) was observed using differential scanning calorimetry (DSC) with thermogravimetric analysis (TGA). The phase transformation temperatures and enthalpies were measured from the alloys annealed at 600 °C for 72, 168, and 672 h. The observations indicated distinctive mismatches between the measured data and the existing U–Zr alloy phase diagram. Most notably, the phase transformation of the (α-U, γ_2) phase to the (β-U, γ_2) phase at ~662 °C was not evident in Zr-rich (> 10 wt%) U–Zr alloys, while only two phase transformations were evident in the U–10Zr and U–20Zr alloys compared to the three isotherm lines extended over the two compositions in the current phase diagram. The absence of the phase transformation is rather consistent with the older U–Zr phase diagram that was experimentally assessed in the 1950s. This observation may lead to the conclusion that the (β-U, γ_2) phase region is not correctly represented in the Zr-rich portion, or the hyper-monotectoid region, of the current U–Zr alloy phase diagram. It is evident that the phase diagram needs to be experimentally revisited to provide more reliable information for the development of metallic nuclear fuel performance models, if such models are to include phase-relevant effects, such as fuel constituent redistribution and fission gas swelling.

1. Introduction

Uranium–zirconium alloys are metallic nuclear fuels and the U–10Zr alloy has demonstrated excellent performance up to ~20 at% burnup with a given ~75% smear density and enlarged cladding plenum in the Experimental Breeder Reactor II (EBR-II) [1,2]. The fuel element design was adopted to accommodate fission gas within the fuel elements at high burnup without significant fuel-cladding mechanical and chemical interactions (FCMI and FCCI). Post-irradiation examinations of high burnup U–Zr and U–Pu–Zr alloys revealed significant restructuring [3–5]. The observed features include a radial phase morphology within the pins related to the temperature profile. The outer (cooler) zones of the pins were clearly comprised of α-U and δ-UZr_2 structures with fine fission gas bubbles, whereas the central (hotter) zones were comprised of γ-U with very large fission gas bubbles. Other features of this restructured fuel included intermediate phases and elemental zirconium gradients. Anisotropic fuel swelling was also observed primarily due to the large interconnected gas bubbles in the hotter central region where the γ-U phase dominates the structure. The bubbles generate biaxial mechanical stress on the annular fuel periphery comprised of the α-U and δ-UZr_2 phase mixture. Smaller bubbles in the outer lower temperature regions also contributed to swelling. Therefore, it is clear that the phase morphology has a significant impact on the fuel behavior, and thus, a precise and accurate understanding of the binary U–Zr phase diagram and relevant thermophysical parameters is required for the accurate prediction of fuel performance.

These phase-dependent fuel restructuring behaviors, swelling and fuel constituent redistribution, need to be reliably accounted for in the modeling of the metallic nuclear fuel performance to predict the eventual fuel/cladding failure. Therefore, a reliable phase diagram of the U–Zr binary system is essentially required to develop a mechanistic fuel performance code. Moreover, to more precisely designate the locations of the boundaries between the phase zones in the fuel pins, the kinetic phase transformation behavior of the alloy on cooling, heating, and long-term annealing is also preferred to be known. However, the presence of fission products and radiation could complicate the validity of this type of kinetic approach. The existing metallic fuel performance codes thus prefer to either refer to the phase diagram for this purpose [3–6] or even assume a homogeneous medium for the entire fuel pin [7–18].

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There have been many efforts in the construction of the U–Zr binary phase diagram using thermodynamic calculative methods and experimental data measurements [19–24]. However, over the last two decades, basically no paradigm shift has been made in the basic features of the current U–Zr phase diagram shown in Fig. 1 [25]. The current phase diagram was constructed based on the selected experimental data available in the late 1980s, and there were some notable conflicts in the data set at the moment. One notable point is that the phase diagram does not show any experimental data supporting the existence of the isotherm line at 662 °C splitting the (α-U, γ_2) and the (β-U, γ_2) phase zones.

This isotherm line at the temperature of 662 °C was mandated by adopting eutectoid decomposition of the β-U phase into the (α-U, γ_2) phase. This feature was first suggested by the measurements of the phase transformation temperatures using dilatometry, although several compositions of the U–Zr alloys exhibited no phase transformation at 662 °C during heating [26]. In the previous study, which was conducted in the mid-1950s, this temperature was measured only once during cooling for the alloy where hysteresis may significantly alter the phase transformation temperature; such hysteresis was self-evident in the study. Another study utilizing differential thermal analysis (DTA) to observe the phase transformations was also referred to the construction of the current phase diagram to support the isotherm line [27]. However, the published DTA data do not clearly confirm the transformation at 662 °C due to the lower resolution of the method.

The older phase diagram published in the late 1950s adopted the peritectoid formation of the α-U phase from the (β-U, γ_1) phase, as shown in Fig. 2 [28]. Therefore, the phase transformation temperatures of α-U to β-U were increased along with increases in the Zr composition of the alloy within the solubility limit of zirconium into uranium, which agrees with the experimental data [29]. Thus, the wide (β-U, γ_2) phase zone is absent from the phase diagram, and the limited (α-U, γ_1) phase zone appeared, as shown in Fig. 2.

This study is a thermophysical investigation to evaluate which phase diagram, between the current and old U–Zr phase diagrams shown in Figs. 1 and 2, respectively, is more consistent with the experimental data measured using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA); i.e., the numbers, temperatures, and enthalpies of phase transformations of the U–Zr alloys, including 0.1, 2, 5, 10, 20, 30, 40, and 50 wt% zirconium; the more consistent phase diagram is more reliable to be referred to simulating the in-file behavior of a metallic alloy nuclear fuel pin subjected to a high temperature and steep radial temperature gradient, thus exhibiting many radial phase zones.

2. Materials and methods

2.1. Alloy preparation

To fabricate the uranium alloys, including 0.1, 2, 5, 10, 20, 30, 40, and 50 wt% zirconium, high-purity zirconium crystal bars and nitric acid-washed depleted uranium chunks were melt-cast in cylindrical yttrium oxide crucibles at ~1900 °C for 1 h, followed by cooling in a furnace to 25 °C at a rate of 30 °C/min under an argon atmosphere using a high-temperature furnace. The cast alloy slugs were flipped and re-melted under identical conditions to improve the homogeneity of the alloys. The resulting dimensions of the cylindrical alloy slugs were ~15 mm both in length and diameter [30].

2.2. Alloy characterization

The melt-cast U–Zr alloys were sectioned to be ~1-mm thick buttons and wrapped with tantalum foils to be subsequently annealed in a quartz tube sealed after evacuation down to 10^{-3} Torr. The as-cast and alloys annealed for 72, 168, and 672 h were examined using a Cameca SX-50 electron probe micro-analyzer (EPMA) equipped with an energy dispersive spectrometer (EDS) and a wavelength dispersive spectrometer (WDS).

The phase transformation temperatures and enthalpies were measured from the characterized alloys by using a DSC–TGA (NETZSCH STA-409PC). The annealed U–Zr alloy buttons were sectioned into 10–100-mg pieces having a flat surface to facilitate a tight contact with the yttrium oxide crucible placed on the DSC sensor platform. The DSC chamber was evacuated immediately after sample loading and then backfilled with 99.9% argon gas, which was further purified using a moisture/oxygen trap system. The loaded alloy samples were heated from 25 °C to 1000 °C at a rate of 5 °C/min.

The DSC was calibrated using the measured melting temperatures and heats of fusion of the seven standard materials of In, Bi, Sn, Zn, Al, Ag, and Au (produced by NETZSCH). The calibration was repeated three times, which resulted in virtually identical standard calibration files for the temperature and enthalpy measurements. To strengthen the validity of the calibration, the phase transformation of uranium was traced using the generated calibration files. The measured phase transformation temperatures and enthalpies of uranium were well matched with the known values [31].

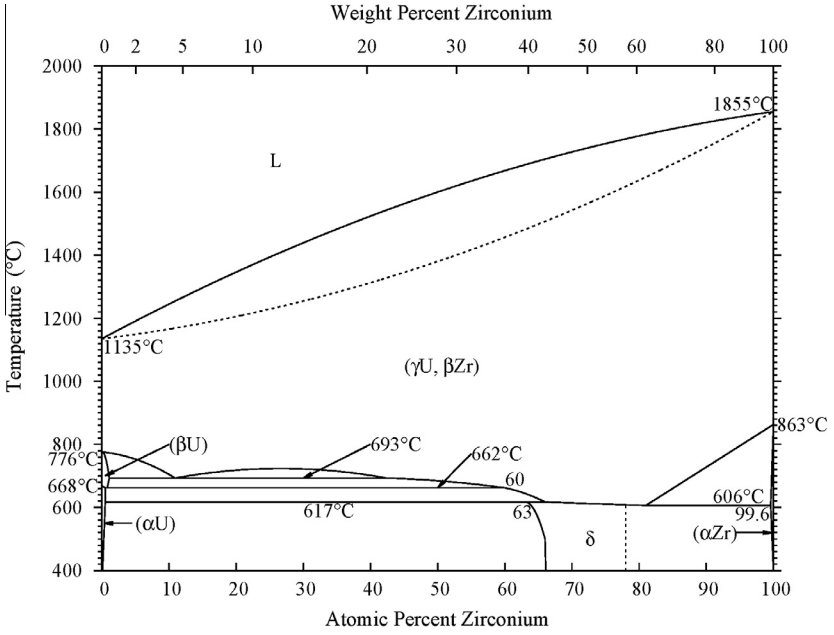

Fig. 1. U–Zr binary phase diagram constructed by Sheldon and Peterson in the late 1980s [25].