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Thermophysical Investigation of Uranium-Zirconium Alloy Phase Diagram

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1. Introduction

Uranium-zirconium alloy system has been studied for over half a century for nuclear applications. Uranium rich part of its binary phase diagram has frequently been investigated mainly due to its promising performance as metallic nuclear fuel. However, the agreement on its phase diagram has not been completely made since experimentally reported peritectoid reaction of ($\beta \leftrightarrow \alpha + \gamma_2$) and eutectoid reaction of ($\beta + \gamma_1 \leftrightarrow \alpha$) are conflicting to each other [1, 2]. In this study transformation start temperatures (T_s) and enthalpies (ΔH) of annealed U-Zr alloys (U-2, 5, 10, 20 and 50wt.%Zr) were measured by differential scanning calorimetry (DSC) and discussed with phase diagrams including either peritectoid or eutectoid reaction.

2. Experimental Methods and Results

Alloy fabrication and characterization methods are described in this section. Experimental procedure of DSC measurements of the U-Zr alloys is also given with analyses on obtained results.

2.1 U-Zr Alloy Fabrication

Depleted uranium (DU) and zirconium pieces were melt casted at 1900℃ in yttrium oxide crucibles under argon atmosphere given aforementioned compositions of U-Zr alloys. Casted alloy slugs were then flipped and again melted under same condition but in slightly larger crucibles in order to improve homogeneity. Formed alloys were cooled at 30℃/min.

2.2 Sample preparation

The U-Zr alloy slugs were sectioned to form 1mm thick buttons. The alloy buttons were then annealed at 600℃ for 700hours in quartz tube under vacuum. Several 10 to 100mg alloy samples were cut from annealed alloy buttons and used for DSC measurements. The nearest adjacent pieces of the identical alloy buttons to DSC samples were characterized using an electron probe micro-analyzer (EPMA) with energy dispersive spectrometer (EDS) and wavelength dispersive spectrometers (WDS). DSC samples were assumed to have comparable chemical compositions and equivalent micro crystal structures with EPMA samples.

2.3 DSC measurement

The DSC system (NETZSCH-409PC) was calibrated using a set of standard materials (In, Sn, Bi, Z, Al, Ag, and Au) for temperature and sensitivity. Transformation enthalpies and temperatures of uranium and zirconium were also measured to reaffirm the calibration, shown excellent reproducibility and matches with reference [3]. Baseline was measured using empty crucibles with lids to compensate possible interference from the system. Sample oxidation was minimized by using high purity argon gas (99.9%) atmosphere passing through an oxygen and moisture trap for the DSC system. The flow rate of purified argon gas was kept at 50ml/min. U-Zr samples were heated to 1000℃ from room temperature. Heating rates were 50℃/min up to 450℃ and 5℃/min up to 1000℃, respectively.

2.4 Results

The measured transformation start temperatures and enthalpies are listed in Table 1. The transformations are referred as 1, 2 and 3 in the order of low temperature. Transformation 1 is apparently (α, δ) → (α, γ_2) reaction and the measured enthalpies of the reaction were significantly smaller than former studies [4]. This may originate from secondary phase formation due to impurity insertion, likely nitrogen and oxygen, during annealing. The measured transformation start temperatures are not completely matched with the widely used U-Zr phase diagram shown in Fig. 1 [2]. Those would rather agree with the older U-Zr phase diagram shown in Fig. 2 [1].

Table I: Measured transformation start temperatures of U-Zr alloy system (T_s uncertainty estimated as ±5℃)

Alloy Comp. (wt.%)	No.	Measured		Modified		Reference		
		T_s (°C)	ΔH (J/g)	ΔH (J/g)	ΔH (kJ/mol)	ΔH_{ref} (kJ/mol)	$\Delta H/\Delta H_{ref}$ (%)	Aurthor (Year)
U-2Zr	1	600	0.26	0.26	0.06	0.32	19.0	Akabori (1995)
	2	673	9.36	9.47	2.23	-	-	-
	3	708	15.50	15.76	3.71	-	-	-
U-5Zr	1	595	2.80	2.84	0.65	0.94	69.7	Akabori (1995)
	2	674	8.66	8.85	2.04	-	-	-
	3	705	16.50	16.96	3.91	-	-	-
U-10Zr	1	570	1.65	1.67	0.37	1.57	23.7	T Matsui (1989)
	2	686	11.63	11.93	2.66	1.43	186.3	
	3	701	4.28	4.39	0.98	0.29	-	
U-20Zr	1	600	12.61	13.08	2.73	-	-	-
	2	688	14.32	15.04	3.14	-	-	-
	3	-	-	-	-	-	-	-
U-50Zr	1	600	34.03	34.37	5.66	5.17	109.4	Akabori (1995)

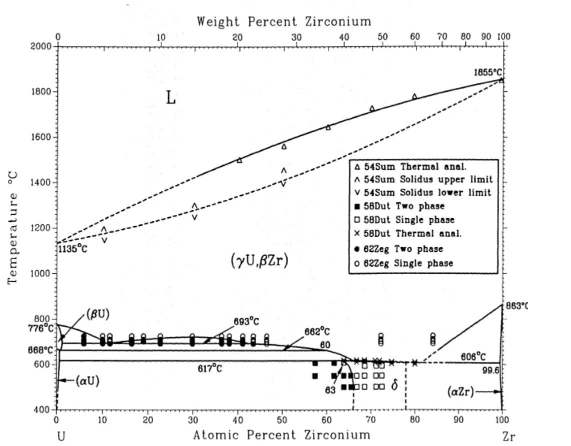

Fig. 1. Assessed U-Zr phase diagram based on eutectoid reaction of ($\beta \leftrightarrow \alpha+\gamma_2$) with resulted wide ($\beta+\gamma_2$) phase field [2]

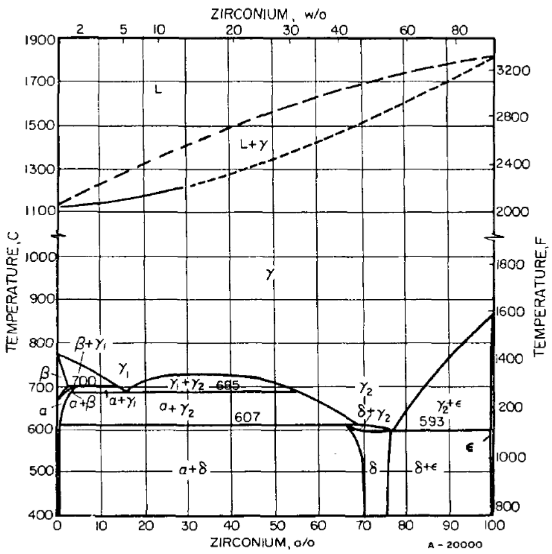

Fig. 2. U-Zr phase diagram based on peritectoid reaction of ($\beta+\gamma_1 \leftrightarrow \alpha$) with resulted narrow ($\alpha+\gamma_1$) phase field [1]

In addition to transformation temperature mismatches, only two transformations observed from U-20Zr clearly indicate the absence of wide ($\beta \leftrightarrow \alpha+\gamma_2$) as shown in Fig.3. Third peak observed in U-10Zr could be originated from ($\alpha+\gamma_1$) phase since extension of the phase field to zirconium rich direction due to relatively higher concentration of impurities was reported [2]. Moreover, size of the peak was notably fluctuating sample by sample. No peak corresponding to the immiscibility gap of ($\gamma_1+\gamma_2$) had appeared. This may be resulted in accordance with its significantly smaller transformation enthalpies [5] and insufficient measurement resolution of used DSC. Transformation 2 start temperatures had distinctively shown a tendency to slightly increase along zirconium composition of the U-Zr alloys, questioning reliability of the isotherm line, however, relatively rapid oxide layer formation of Uranium rich alloys is speculated as an underlying principle for the phenomenon. Synthetically, the DSC data denote further investigation on the U-Zr phase diagram is required to improve its reliability.

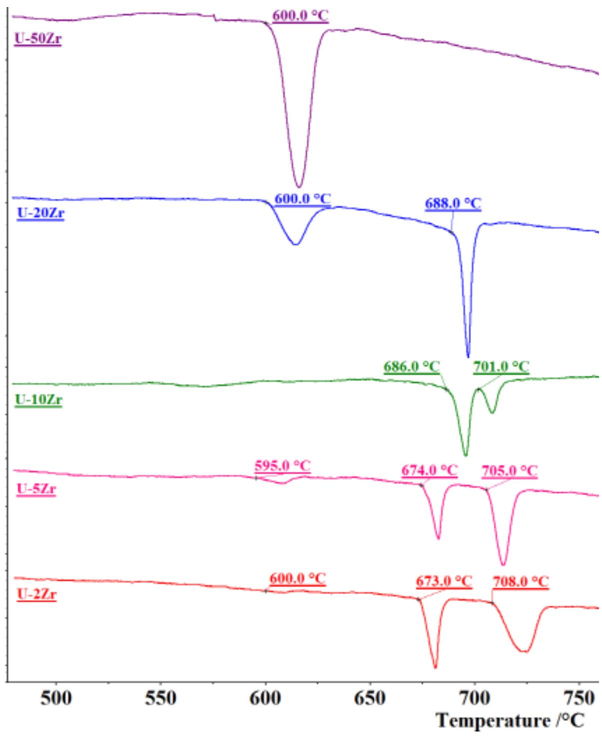

Fig. 3. DSC heating curves of U-2, 5, 10, 20 and 50Zr alloys, annealed for 700hours at 600℃

3. Conclusions

General mismatches between obtained transformation temperatures from DSC measurements and widely used U-Zr phase diagram imply that the U-Zr alloy phase diagram needs to be revisited. Unmatched number of transformations has been found from U-20Zr alloy strengthen the necessity. It requires, however, more experimental data.

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