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Thermomechanical Processing of Uranium Alloys with 10 and 50 Weight Percent Zirconium

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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99354

Abstract

This work focuses on casting and thermomechanical processing for moderate sized (500-1000g) 10% by weight and 50% by weight uranium-zirconium alloys. Three castings of uranium – 10wt% zirconium and a fourth casting of uranium – 50wt% zirconium were completed using different castings processes. The first casting process relied on only induction mixing within the VIM system thereby eliminating the need for an arc-melting feedstock preparation step. The second casting process used the arc-melting process prior for feedstock to the same VIM system. In this study, the induction mixing process alone with a graphite crucible appears insufficient for the fabrication of UZr alloys. Graphite is suitable with the use of master alloy UZr feedstock produced by arc-melting. There was a moderate increase of approximately 100 ppm of carbon within the U10Zr alloys. However, there was a near 1000 ppm increase of carbon in the U50Zr alloy. This carbon content is considered too high for forming processes, and therefore, warrants the use of a ceramic crucible for UZr castings near 50wt% zirconium. Zirconia does not appear suitable for UZr castings near 50wt% zirconium. The use of Beryllia or Thoria may be a more suitable option. However, due to the significantly lower liquidus and lower zirconium content, Zirconia crucibles do appear viable for carbon reduction in the U10Zr system. Two thermomechanical processes are also studied in this work - hot extrusion of the U50Zr system and heat treatment in an argon atmosphere. This work demonstrated that extrusion of the U50Zr alloy near 680°C is a viable choice even with +1000 ppm carbon. Extrusion of the U50Zr system near 630°C was unsuccessful and does not appear viable unless significant force and tooling strength is available. There appears to be a moderate increase in extrudate hardness when compared to as-cast. Heat-treatment reduced the hardness of as-cast alloys in the U10Zr castings as well as resolve some variance in the microstructures. However, for the U50Zr billet that did not successfully extrude at 630°C, heat treatment at 900°C for 96 hours did not have a significant impact on hardness or microstructure.

Acronyms and Abbreviations

BCC	body centered cubic
DI	deionized
DOE	Department of Energy
DU	depleted uranium
EBR	Experimental Breeder Reactor
FCRD	Fuel Cycle Research and Development Program
FFTF	Fast Flux Test Facility
HALU	high-assay-low-enriched-uranium
HCP	hexagonal close packed
ODS	oxide dispersion strengthened
OM	optical microscopy
PNNL	Pacific Northwest National Laboratory
RPL	Radiochemical Processing Laboratory
UZr	uranium-zirconium Alloys
U10Zr	uranium-10 weight percent zirconium
U10ZrPu	uranium-10weight percent zirconium-plutonium
U50Zr	uranium-50 weight percent zirconium
VIM	vacuum induction melting
XRD	x-ray diffraction

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1.0 Introduction

Uranium-zirconium (UZr) metal alloys have been used in nuclear reactors such as the Experimental Breeder Reactors (EBR) I and II, Fast Flux Test Facility (FFTF), and Dounreay Fast Reactor[1–4]. All metal fuels provide many benefits over ceramic fuels. Metal fuels have higher thermal conductivity, higher fissile material density, are compatible with austenitic stainless steel cladding, and corrosive coolants like that of sodium[1–4]. Furthermore, the conversion of high-enriched uranium oxide fuel to that of low-enriched metal fuel along with the use of pyroprocessing as a metal recovery method is seen as a reduced proliferation concern. However, there are challenges with the fabrication of UZr metal fuels.

Due to the reducing properties of molten zirconium, high purity, phase consistent UZr feedstock can be a challenge to produce. High levels of carbon (>500 ppm) and inclusions with very low actinide solubility (<1%) such as carbon, oxygen, and/or nitrogen-stabilized alpha phase zirconium are common issues with UZr fabrication. Typically, vacuum induction melting (VIM) is used to produce uranium alloys on a kilogram-scale. Graphite crucibles and molds are commonly used in VIM systems, especially when the liquidus of an alloy is near 1600°C as is with the greater than 30% w/w UZr alloys. However, the production of a homogenous alloy can be difficult in a VIM system as induction mixing with a graphite inductor can be deficient. Furthermore, thermomechanical processes often subject as-cast alloys to multi-phase temperature profiles that increase multiphase microstructural regions.

Ceramic crucibles provide transparency in a VIM induction field allowing for magnetic coupling directly to the feedstock thereby increasing induction mixing of constituents. However, few ceramics can withstand the temperature, thermal shock, and reducing environment of the molten high Zr uranium alloys. Therefore, non-consumable arc-melting is typically used to form UZr master alloy feedstocks for the VIM process. This multi-step production method increases cost as well as the potential for additional impurities in the final product.

Furthermore, modern UZr fuel designs typically require thermomechanical processing to achieve phase homogeneity and final fuel form. In the past, as-cast microstructures were seen as preferential. Fuel pins for the EBR cores were used as injection cast uranium-10 wt.% zirconium-plutonium (U10ZrPu) alloys to reduce texture. Prior to this "as-cast" method, the texture in EBR fuels pins allowed for an undesirable irradiation induced grain growth.[1,5] It is recognized that heat treatments can randomize crystallographic texture therefore reducing the preferential texture associated with some processes.

In order to explore properties of the UZr binary system, the Pacific Northwest National Laboratory (PNNL) has arc melted, cast, heat treated, and extruded U10Zr (nominal) ($\alpha U + \delta UZr_2$) and U50Zr (nominal) (δUZr_2) alloys. Two U10Zr ingots[1] were attempted with the VIM process alone, and two UZr (one U10Zr and one U50Zr) ingots were produced with a combination of non-consumable arc melting and VIM processes. Furthermore, two arc melted "buttons" were produced outside the casting process to analyze the pre-VIM master alloys. PNNL bisectioned the U50Zr ingot for extrusion, one billet[2] was for extrusion at 630°C and one billet for a 680°C extrusion. This was done in an attempt to examine the extrusion force required of the γU-βZr two phase billet vs the δUZr single phase billet. Although 630ºC is above the phase boundary, 630ºC was chosen to achieve maximum billet temperature near the γU-βZr

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[1] Ingot is used in reference to the as-cast geometry of the alloy

[2] Billet is used here to reference the alloy post-modification from its as-cast geometry

phase boundary. The choice was made with consideration of billet cooling during manual transfer from furnace to press as well as additional cooling from billet contact with press tooling (the dummy block was preheated but loaded prior to the billets). Furthermore, billet preheat time was only 2 hours in air. The extrusion at 680°C was successful. The extrusion at 630°C was not successful. Additionally, heat treatment of UZr was performed. This report summarizes the results of these experiments.

2.0 Casting Methodology and Materials

PNNL's prior experience with U binary and ternary alloy systems highlighted the need for master alloy formation via arc melting prior to the VIM process. However, PNNL conducted two U10Zr (nominal) castings (first and second casting) without prior master alloy formation to explore induction mixing with an Indutherm VTC200Ti VIM and a graphite crucible. The induction system operates at a relatively high frequency (approximately 15 kHz), therefore, it was known that significant penetration of the induction field beyond the walls of the graphite crucible (>1/8") would be limited.

For the VIM-only ingots, the crucible was loaded into the VIM with a mixture of DU and Zr metal (Zr on bottom, DU on top). This did not produce satisfactory ingots. The ingot process data and casting parameters are shown in Tables 2.1 and 2.2, respectively. Images of the primarily U billets and crucible dross (primarily zirconium) are shown in Figure 2.1 for the first ingot, and Figure 2.2 for the second ingot. The third and fourth ingots were produced with UZr master alloys. These were successful. The casting parameters are shown in Table 2.2. Images are shown in Figure 2.3 (#3 - U10Zr) and 2.4 (#4 - U50Zr).

The U10Zr and U50Zr alloys were produced in the Radiochemical Processing Laboratory (RPL) at PNNL with depleted uranium (DU) from Aerojet Rocketdyne in Tennessee and Alfa Aesar supplied zirconium slugs (99.5% basis with 3% hafnium). The DU was supplied as plates, approximately 1.25" x 1.25" x 0.2" in size. The plates were reduced by shearing to approximately 1.25" x 0.5" x 0.2" sections. The zirconium was supplied as approximately 0.125" diameter x 0.25" slugs. Alloying was achieved using a VIM furnace and a non-consumable electrode arc-melter. The VIM used was an Indutherm VTC-200Ti tilt-pour casting system. The non-consumable arc melting system used was an Edmund Bühler GmbH Compact Arc Melter MAM-1. Before use, the stock DU was etched for 10 minutes in 8 molar nitric acid to remove oxidation, rinsed in deionized (DI) water, followed by a final rinse in ethanol to remove residual water. The zirconium was rinsed in ethanol. The DU and zirconium were alloyed within four hours of the etching process.

A 1.75" inner diameter x 6.0" tall graphite crucible and a 1.20" inner diameter x 8.0" tall right cylinder graphite mold was used for ingot fabrication. The crucible and mold were cleaned between each casting by sonication for 10 minutes in DI water; then dried in an air atmosphere muffle furnace for approximately 24 hours prior to coating with Yttria (Y_2O_3). The purpose of the inert coating was to prevent molten uranium and/or zirconium from interacting with the graphite crucible and/or mold. Inert coatings are known to reduce the carbon content from melt-graphite interactions in the final uranium alloy products. Yttria supplied by ZYP Coatings was dispensed from aerosol cans onto the warm graphite (~50-100°C) crucible and mold in 3 thin layers. Between each coating, the crucible and mold were dried in a muffle furnace between 150-200°C for a minimum of 1 hour.

After the coating was cured and with the crucible near room temperature, the crucible was charged with the UZr constituents so to not scratch the Yttria. For the U10Zr ingots cast without master alloy feedstock, the charge was DU plates and Zr slugs. For the U10Zr and U50Zr ingots cast with master alloy feedstock, the charge was arc melted UZr "buttons". Alumina encased nichrome resistance heaters were attached to the outside surfaces of the mold with stainless steel bands to provide approximately 350-450°C of mold preheat. The mold preheat attempts to reduce pre-solidification of the UZr melts by reducing the significant temperature gradient between the melt (1450-1850°C) and mold. The atmosphere of the VIM chamber was "washed" by 3 argon/vacuum exchanges for each casting prior to applying power to the induction coil. The castings were all melted and poured in a vacuum atmosphere. For each casting, the crucible and mold power were terminated at the time of pour. The castings are cooled in a vacuum atmosphere for 10 minutes prior to the application of a static argon atmosphere (approximately 1 atmosphere gauge) for final cooling to room temperature. To produce the U10Zr and U50Zr master alloy buttons in a 50g-100g range for the third and fourth castings, the water cooled copper crucible of the arc melter was loaded with sheared DU plate and zirconium slugs. The arc melting was preceded by the same type of 3 argon/vacuum atmosphere exchanges as with castings #1 and #2. However, the buttons were fabricated within an approximately 0.75 atm argon pressure. An approximately 10g piece of zirconium metal was placed separate from the UZr charge within the chamber. This was the first metal melted by the operator to getter any oxygen remaining in the atmosphere. The melting, cooling, rotating, and remelting cycle was performed 3 times for each button. The arc melter operates at high temperatures (~3000°C) during melting. The rotation of the arc increases the efficacy of the U-Zr alloying process by inducing currents within the melt while the high temperatures lower the diffusion barrier. Post-casting, all four ingots were sectioned using a Buehler Abrasimatic 3000. Samples for carbon and metallurgical analyses were taken from the top and bottom of the four as-cast billets. For the U50Zr, the ingot was sectioned into two billets for extrusion. Additional samples for analyses were taken from the top and bottom of the post-extrusion billets. Details for each ingot and sample location are in Table 1.

Table 2.1 U10Zr & U50Zr Process and Sample Data

Casting	Successful	As-Cast Samples	Forged	Forged Samples	Heat Treatment	Post-HT samples
U10Zr #1	No	Top; Bottom	No	N/A	96hrs 900°C	Top; Bottom
U10Zr #2	No	Top; Bottom	No	N/A	No	N/A
U10Zr #3	Yes	Top; Bottom	No	N/A	96hrs 900°C	Top; Bottom
U50Zr #4	Yes	Top; Bottom	#4A;	Top; Bottom	No	N/A
			#4B[1]	Top; Bottom	96hrs 900°C	Top; Bottom

Table 2.2 U10Zr VIM-Only Castings

Casting	DU Mass (g) (nominal)	Zr Mass (g) (nominal)	Crucible Charge Pattern	Maximum Temp (°C)	Hold Time (mins)	Total Time (mins)
U10Zr #1	540	60	Zr bottom; U Top	1500°C	15	25
U10Zr #2	540	60	Intermixed	1600°C	45	65

Table 2.3 U10Zr & U50Zr VIM Castings with Master Alloy

Casting	DU Mass (g)	Zr Mass (g)	Crucible Charge Pattern	Maximum Temp (°C)	Hold Time (mins)	Total Time (mins)
U10Zr #3	810	90	Master Alloy	1500°C	4	7
U50Zr #4	300	300	Master Alloy	1875°C	2	9

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[1] Billet upset in extrusion press above 150 kips therefore was not extruded.

Figure 2.1. U10Zr Casting #1 (VIM-Only) (left: Billet; right: Crucible Dross)

Figure 2.2. U10Zr Casting #2 (VIM-Only) (left: Billet; right: Crucible Dross)

Figure 2.3. U10Zr Casting #3 (Master Alloy Feedstock)

Figure 2.4. U50Zr Casting #4 (Master Alloy Feedstock)

3.0 Extrusion Methodology and Materials

Uranium-zirconium alloys with 10-30 w/w zirconium are well documented for use as nuclear fuel. Arguably, the fuels fabricated for the EBR and FFTF reactors serve as a foundation for the U10-30Zr w/w system. In fast reactors like EBR, as-cast small diameter (3-10mm) fuel pins have been the preferred application. However, for thermal neutron reactor fuels with high-assay-low-enriched-uranium (HALEU < 20% U-235), the uranium-zirconium binary alloy with 42-50 w/w zirconium is of interest. The liquidus of this higher zirconium content alloy exceeds the softening point of the quartz molds that served the 10-30 Zr w/w system. Furthermore, the design of light water reactor all metal fuel rods, like that proposed in Lancaster[6] or contemporarily by Lightbridge[7], will likely require thermomechanical processes such as swaging or extrusion.

Irukuvarghula et al. provides a review of the influence that thermomechanical processing conditions have on the final properties of U10Zr alloys.[8] Irukuvarghula et al. poses an interesting theory about the retention of texture in the δ-UZr$_2$ phase post-transition through multi-phase heat treatments in the U10Zr alloy.[8] This may prove to be relevant to the U50Zr alloy as processing of this system typically occurs above the δ-phase field due to the limited ductility of the δ-phase compared to that of the higher temperature γ-phase.[9] However as a final fuel form, the intermetallic δ-phase is attractive for its equiaxed grain structure and potential for limited, isotropic swelling. There is precedence of good performances with intermetallics in nuclear fuel designs (e.g. UAl$_x$ systems). Limited data has been shown regarding the fabrication, retention, and performance of the U50Zr δ-phase.

In order to explore U50Zr thermomechanical properties, PNNL cast a U50Zr ingot for extrusion above (680ºC *γU+βZr-phases)* and near the δ-phase boundary (630ºC). Although 630ºC is above the phase boundary, 630ºC was chosen to achieve maximum billet temperature near the γU-βZr phase boundary, as there was concern that a billet temperature of less than 650ºC coupled with the hardness of the U50Zr alloy would make for a significant challenge. Also, consideration was given to billet cooling during manual transfer from furnace to press as well as additional cooling from billet contact with press tooling (the dummy block was preheated but loaded prior to the billets). Furthermore, billet preheat time was only 2 hours in air.

PNNL extrusions are made with a custom built 75 ton press located within the Physical Sciences Facilities 3410 building. The dimensions of the two U50Zr pre-extrusion billets were approximately 1.15" OD x 1.125" long each. The 630°C billet contained an approximately 3/16" OD x 1/4" pipe remnant from the pipe in the top of the casting. The defect is shown in Figure 3.1 along with the extrusion billets. The 680°C billet did not contain a pipe. The billets were canned with an approximately 0.020" copper jacket and lubed.

Prior to extrusion, the billets, dummy block, and graphite push block were preheated in an air atmosphere muffle furnace for 2 hours. Both extrusions were scheduled for a near 3:1 reduction ratio. Post-extrusion, the 680°C billet had a final OD of approximately 0.7" (with Cu can). The force curve for the 680°C extrusion is shown in Figure 3.2. Figure 3.3 shows the 680°C extrudate. The 630°C extrusion was not successful. The billet was upset at the die face with approximately 75 tons of force. The leading edge of the billet was chamfered, and the billet was axially compressed. The billet was recovered. The force curve for the 630°C extrusion is given in Figure 3.4. Figure 3.5 shows the upset billet within the copper can. Only the leading edge of the copper can passed into the die, as seen in Figure 3.5.

Figure 3.1 U50Zr 630°C Extrusion Billet and Cu Can (left); 680°C and 630°C Canned Billets with 630°C Billet Lubed (right)

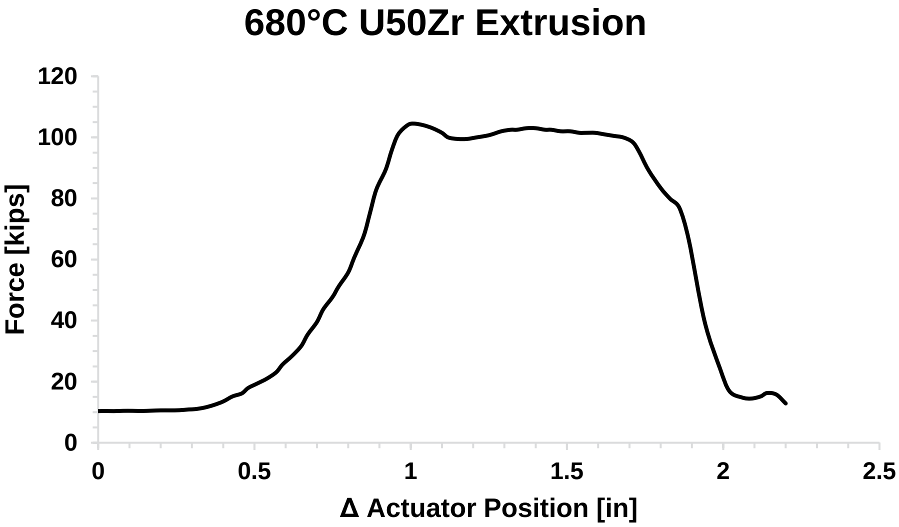

Figure 3.2 680°C Extrusion Force Curve

Figure 3.3 680°C Extrudate (Cu Canned)

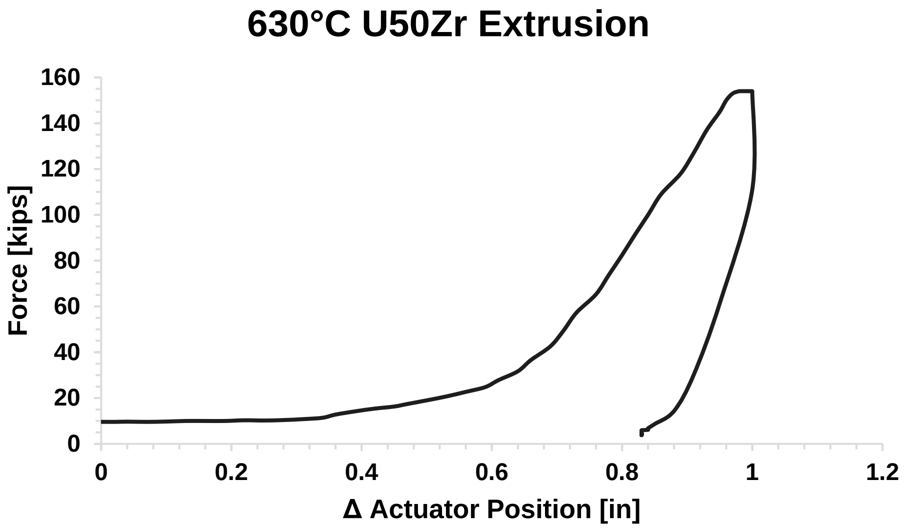

Figure 3.4 630°C Extrusion Force Curve

Figure 3.5 630°C Upset Billet (Cu Canned)

4.0 Heat Treatment

As expected, the U10Zr and U50Zr alloys respond differently to heat treatment. According to the phase diagram, the U10Zr as-cast alloy consists of two-phases (αU and δUZr_2) from room temperature to near 600°C. The U50Zr as-cast alloy consists of one phase (δUZr_2) from room temperature to near 600°C. The U10Zr alloy transforms from $l \rightarrow \gamma U+\beta Zr \rightarrow \gamma' U+\gamma'' Zr \rightarrow \beta U+\gamma'' Zr \rightarrow \alpha U+\gamma'' Zr \rightarrow \alpha U+\delta UZr_2$.[2,10–12] Whereas, the U50Zr alloy simply transforms from $l \rightarrow \gamma U+\beta Zr \rightarrow \delta UZr_2$.[2,10–12] It has been shown that there exists an omega transformation in the delta phase portions of UZr alloys similar to that found with IVB transition metals.[2,3,8] The omega transformation appears predominately in alloys quenched from a body centered cubic (*BCC)* phase, aged in a metastable *BCC* phase, or as a result of irradiation.[13] The omega phase is described as being a disordered version of delta phase as a result of *BCC* instability.[13] This instability results in a hexagonal structure from collapsed *BCC* layers formed through a martensite tranformation.[13]

For the UZr alloys, the omega transformation has been explored for its influence on the formation, texture, and stability of alpha, gamma, and delta phases. Arguably, omega transformation in U-rich UZr alloys has been investigated in greater detail than that of the Zr-rich UZr alloys. This may be due to the Department of Energy's (DOE) Fuel Cycle Research and Development Program (FCRD) focus on the U-rich UZr alloys[14] as well as the high temperatures required to fabricate the Zr-rich UZr alloys.

Irukuvarghula et al. expand on subtleties of the UZr transformation process with an intriguing relationship between phase transformation temperature and crystallographic texture in the U-rich and Zr-rich fractions of U10Zr alloys.[8] In their work, they challenge whether this same relationship is seen in post-forged delta phase Zr-rich UZr alloys.[8] Proper exploration of this topic is beyond the focus of this work. However, as yield strength is related to crystallographic texture, this relationship may provide insight into the U50Zr extrusion temperature.

For the U10Zr alloy, there is significant interest in the fraction of alpha phase vs delta phase, as there is limited solubility of Zr in alpha phase U at room temperature. Furthermore, the phase fraction and particle/agglomerate size of the delta structure in the U10Zr system appears sensitive to solidification rates of as-cast ingots as well as the time and temperature of heat treatment.

In order to compare as-cast vs heat treated U10Zr and U50Zr structures for this work, a single 900°C heat treat for 96hrs was performed in argon to simply analyze any microstructure changes regarding the alpha/delta phase and beta/gamma/delta phase relationships. To that end, Casting #1 (VIM-only U10ZR), Casting #3 (arc-melted+VIM U10Zr), and the post-upset section of Casting #4 (arc-melted+VIM U50Zr) were heat treated in the same 900°C for 96hrs cycle. The post-forged U50Zr billet was of particular interest for its post-anneal hardness.

5.0 Analyses

Single vs two phase primary room temperature microstructures are known as a key difference between the U10Zr and U50Zr alloys. The U10Zr alloy consists primarily of *αU* and δUZr_2 phases at room temperature. The U50Zr alloy consists primarily of the δUZr_2 phase at room temperature. A less abundant feature in both alloys are *αZr* phase precipitates*.* The mechanisms that stabilize *αZr* precipitates appear dependent upon the impurities present during processing. The *αZr* precipitates are generally seen as an impurity stabilized phase (O_2, N_2, C, CO, etc.).[8,15] The main challenge with the *αZr* and *αU* phases is that of solubility because *αZr* has a very low actinide solubility and is a hexagonal close packed (hcp) crystal structure that can exhibit high anisotropic yield strength.

Furthermore, significant impurity-stabilized zirconium precipitates have the potential to increase UZr alloy yield strength, similar to the mechanisms seen in oxide-dispersion-strengthened (ODS) steel alloys. This in turn could require higher thermomechanical processing temperatures and/or higher forming forces. *αU* has a very low zirconium solubility and exhibits anisotropic behaviors with an orthorhombic crystal structure. The δUZr_2 phase is also a hcp structure. These properties illustrate the complexity with the formation of homogenous, predictable uranium-zirconium alloys.

Optical microscopy (OM) was the predominate method of analysis for this work as phase structures of UZr are readily identifiable with this method. Table 5.1 lists the location and pre-processing step for each microscopy sample. Metallography samples were mounted in epoxy and polished to 1 µm surface roughness using a combination of silicon carbide sandpapers, followed by diamond suspensions, and finished on a vibratory polisher using a colloidal silica solution prior to chemical etching. The etchant was a mixture of nitric and hydrofluoric acids diluted with water.[16] The cross section of each ingot/billet was imaged. The micrographs are shown in Figure 5.1-5.16.

Further analyses included hardness and carbon content. Hardness is a key parameter for the UZr alloys and is relatable to the carbon as well as zirconium content. Rockwell C hardness is presented in Table 5.2. Carbon content was evaluated with a LECO C analyzer and is presented in Table 5.3.

Table 5.1 U10Zr and U50Zr Microscopy Sample Locations

Casting	Arc Melt Feedstock	As-Cast Samples	Post Forged Samples	Post-HT samples
U-10Zr #1	N/A	Top; Bottom	N/A	Top; Bottom
U-10Zr #2	N/A	Top; Bottom	N/A	N/A
U-10Zr #3	Edge	Top; Bottom	N/A	Top; Bottom
U-50Zr #4	Edge	Top; Middle	#4A -Top; Bottom	N/A
			#4B[1] - N/A	Top; Bottom

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[1] Billet upset in extrusion press above 150 kips therefore was not extruded.

Table 5.2 U10Zr and U50Zr Rockwell C Hardness

Sample	HRC1	HRC2	HRC3	HRC4	HRC 5	HRC6	HRC Avg	Std Error of Mean
U-10Zr #1 Top As-Cast	34	36	41	25	26	37	33.2	2.60
U-10Zr #1 Bottom As-Cast	41.5	43.5	43	45	42	43.5	43.1	0.51
U-10Zr #2 Top As-Cast	32	41	41.5	35	33	37	36.6	1.64
U-10Zr #2 Bottom As-Cast	39.5	38.5	41	41	40	42	40.3	0.51
U-10Zr #1 Post-Heat Treated	40	39.5	40.5	41	41	40.5	40.4	0.24
U-10Zr #3 As-Cast	27	39	48	42	46	46	41.3	3.16
U-10Zr #3 Post-Heat treated	36	33.5	32.5	29.5	30.5	29	31.8	1.09
U-50Zr #4 As-Cast	27	30	30	30.5	24	32.5	29.0	1.23
U-50Zr #4A Extrudate	36	34	37	37	36.5	36	36.1	0.45
U-50Zr #4B Upset Billet Post-Heat Treated	29	29.5	24	30.5	29	N/A	28.4	1.13

Table 5.3 U10Zr and U50Zr Carbon Content

Sample	Carbon ppm
U-10Zr #1 Top	384
U-10Zr #1 Mid	440
U-10Zr #1 Bottom	484
U-10Zr #2 Top	454
U-10Zr #2 Mid	511
U-10Zr #2 Bottom	221
U-10Zr #3 Top	835
U10Zr #3 Bottom	711
U-50Zr #4 Top	1832
U-50Zr #4 Mid	1256
U-50Zr Arc Melt	579
U-10Zr Arc Melt	694
Aerojet DU	536

Zr Slug	218

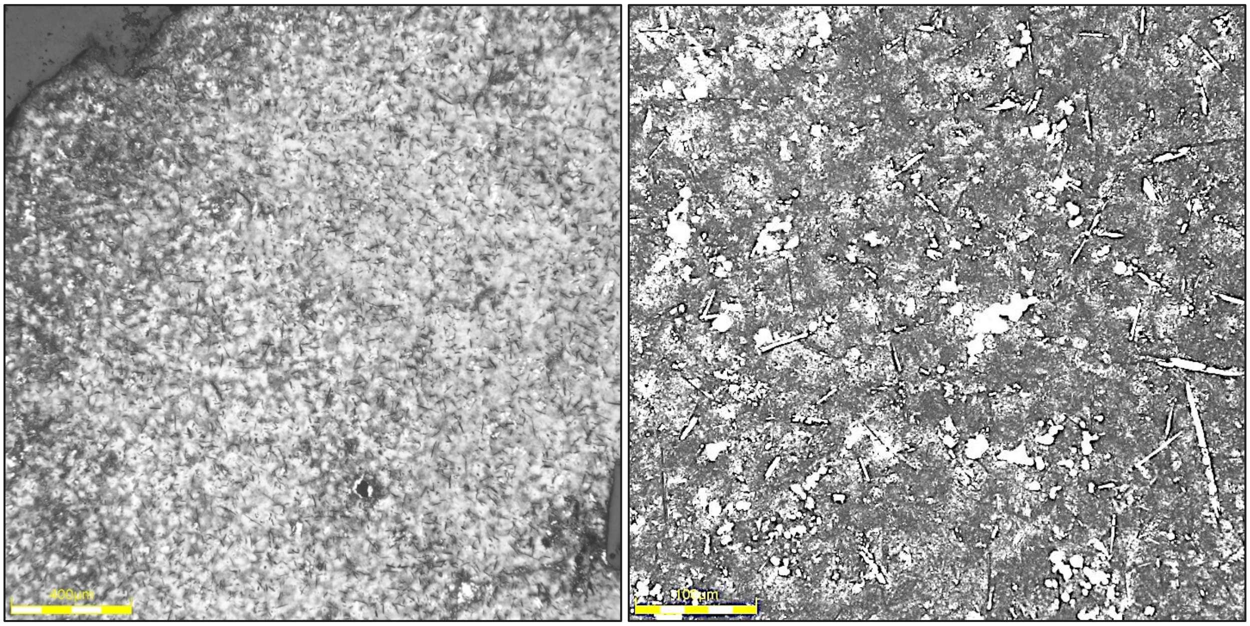

Figure 5.1: U-10Zr #1 Top As-Cast Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

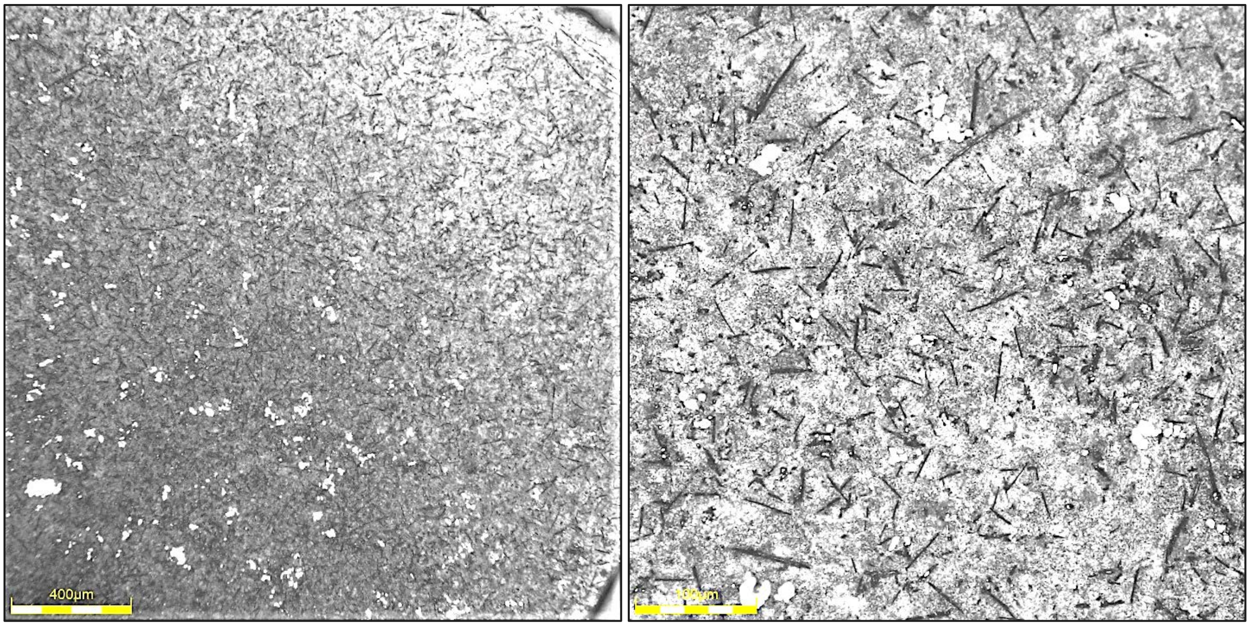

Figure 5.2: U-10Zr #1 Bottom As-Cast Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

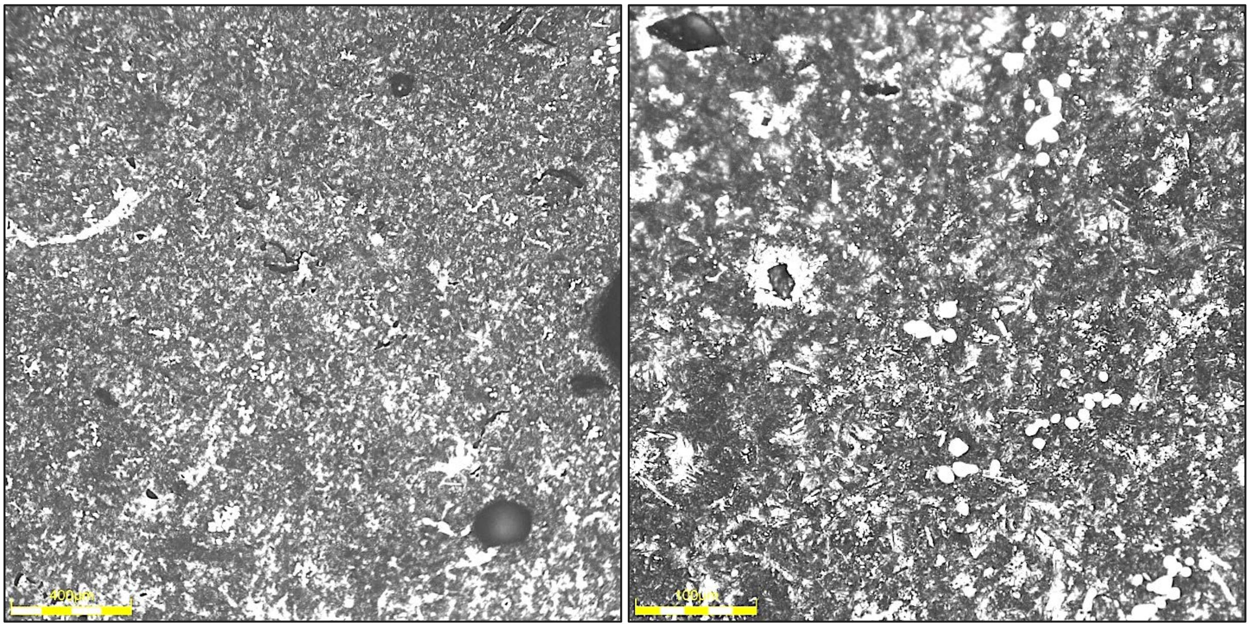

Figure 5.3: U-10Zr #2 Top As-Cast Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

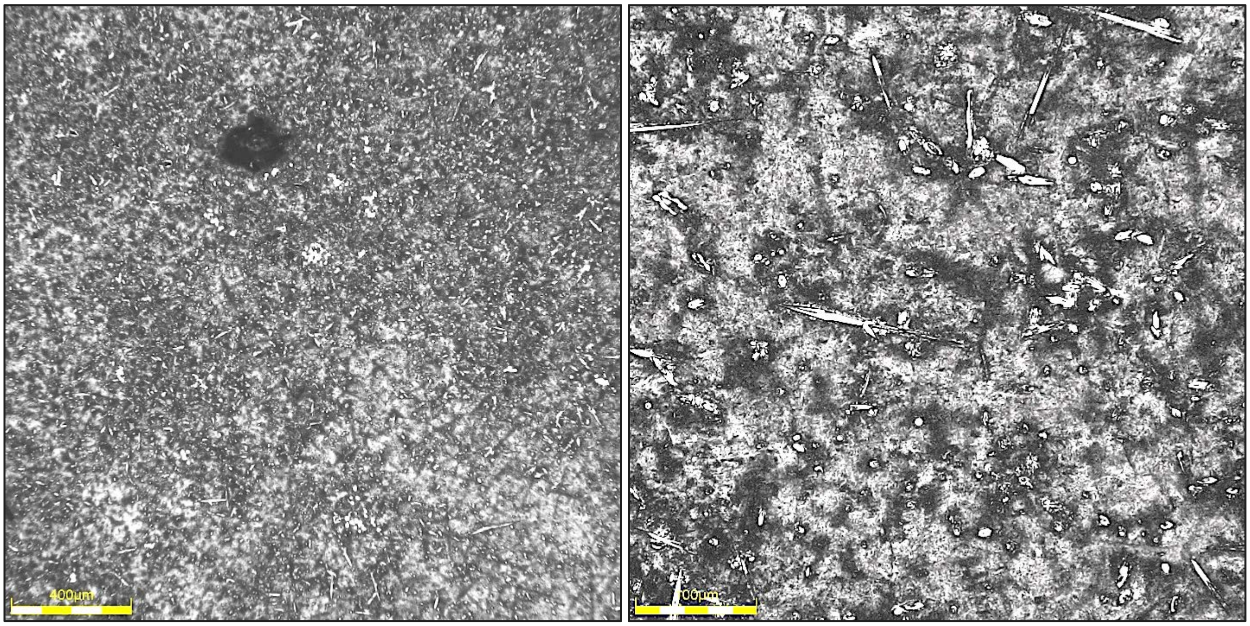

Figure 5.4: U-10Zr #2 Bottom As-Cast Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

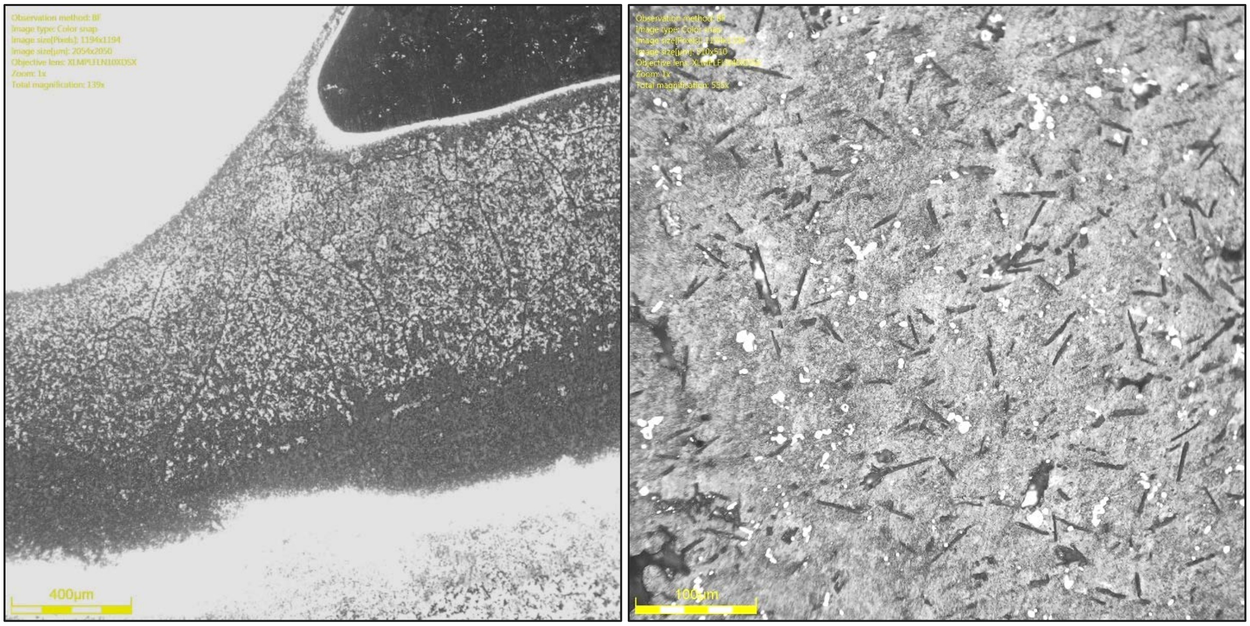

Figure 5.5: U-10Zr #3 Top As-Cast Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

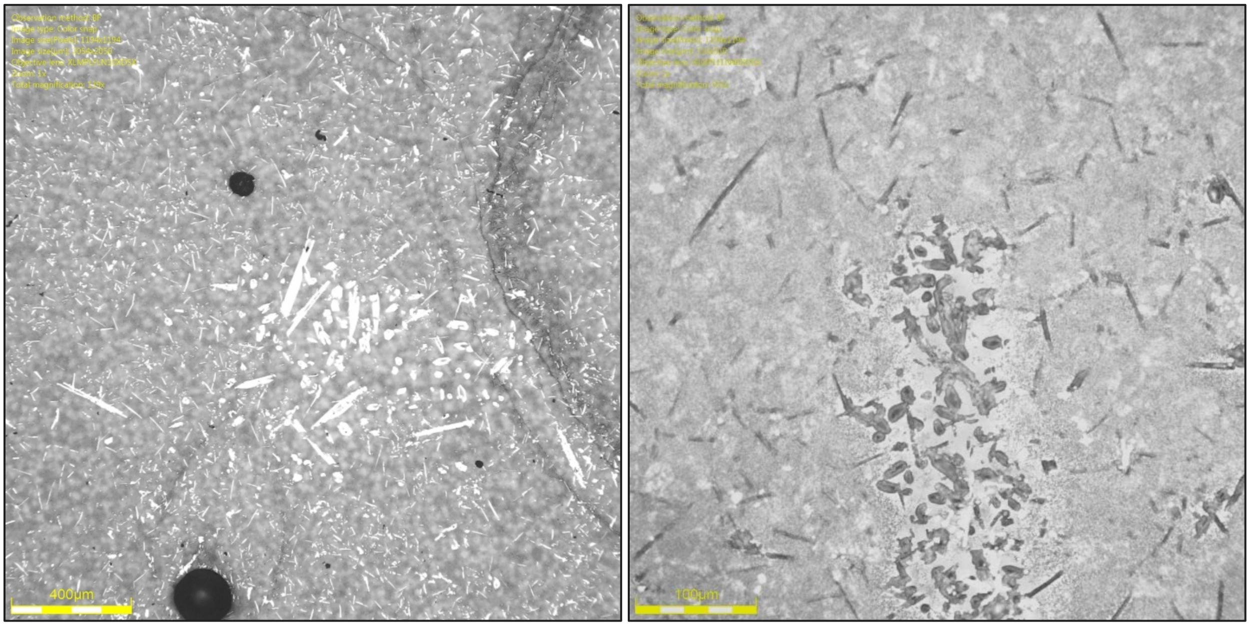

Figure 5.6: U-10Zr #3 Bottom As-Cast Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

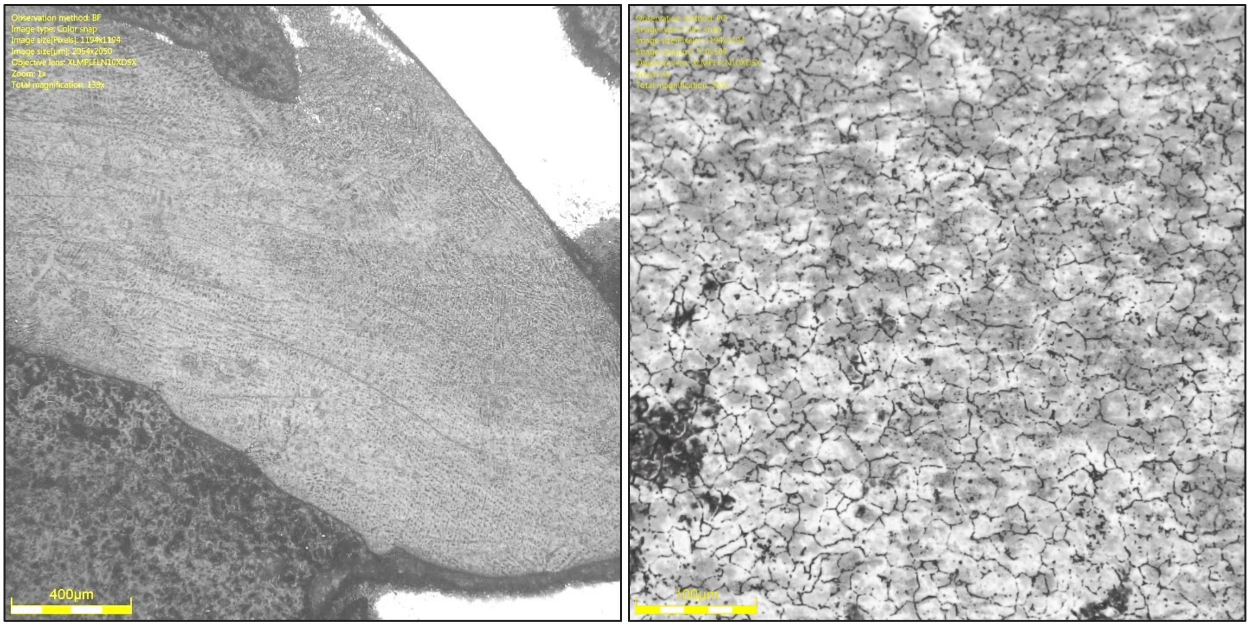

Figure 5.7 U-10Zr Arc Melted Feedstock Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

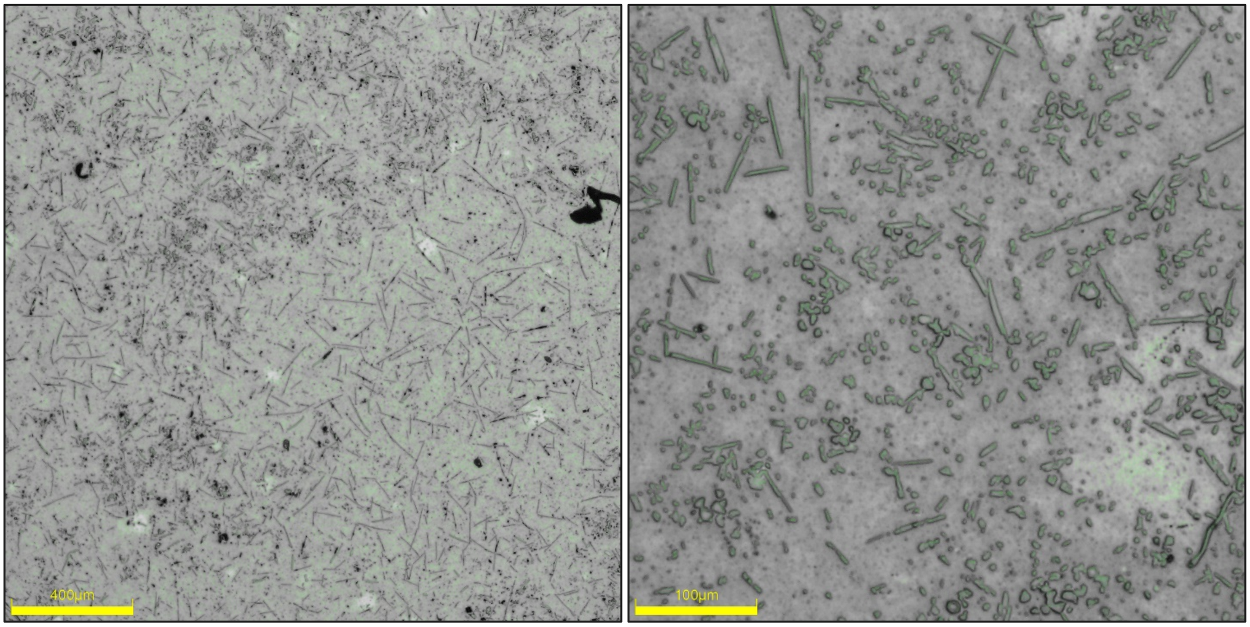

Figure 5.8 U-10Zr #1 Heat Treated Top 96hr 900°C Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

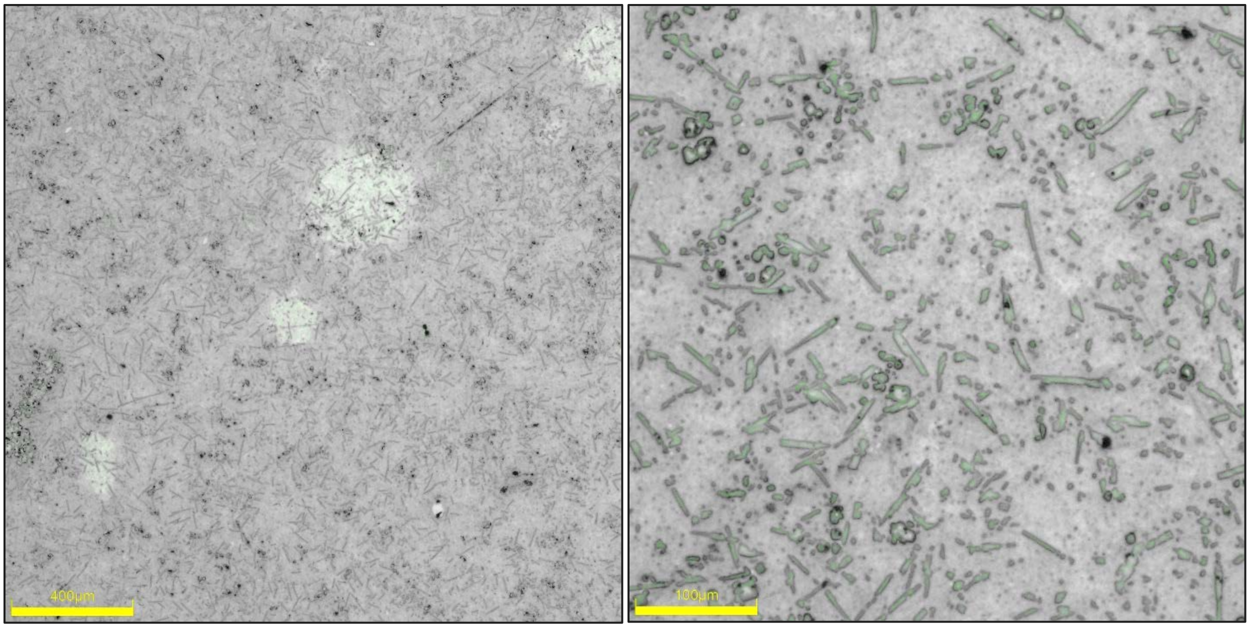

Figure 5.9 U-10Zr #1 Heat Treated Bottom 96hr 900°C Micrograph (left: 139x, right: 555x). Scale bar is 400μm and 100μm, respectively

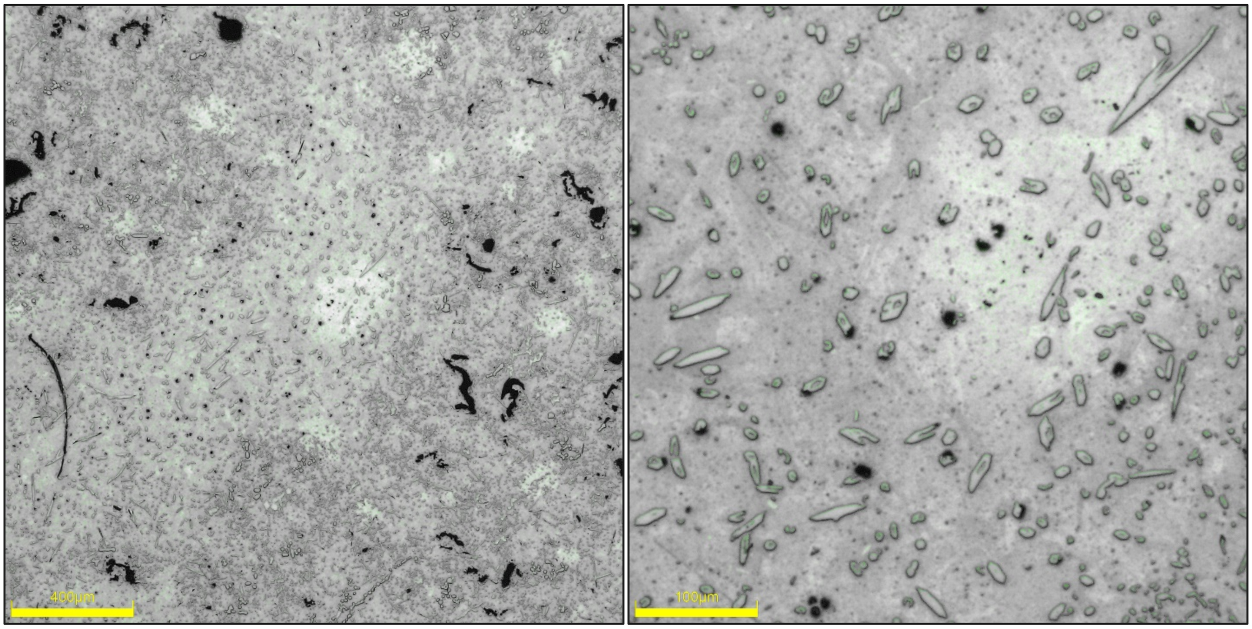

Figure 5.10 U-10Zr #3 Heat Treated Top 96hr 900°C Micrograph (left: 139x, right: 555x). Scale bar is 400μm and 100μm, respectively

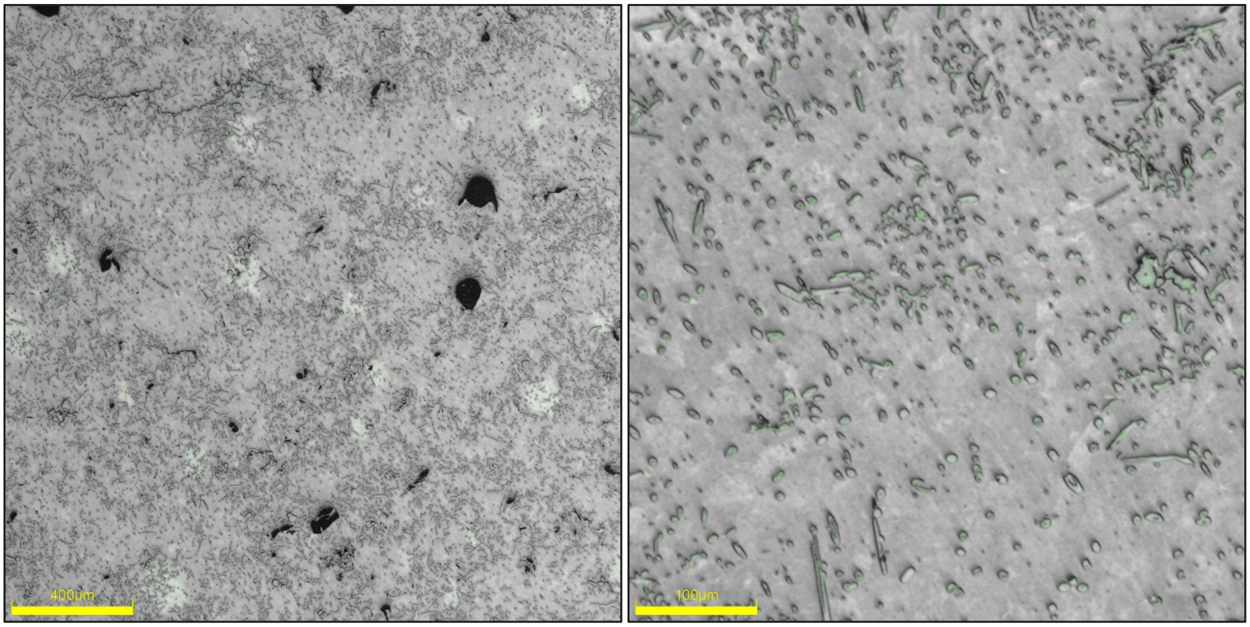

Figure 5.11 U-10Zr #3 Heat Treated Bottom 96hr 900°C Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

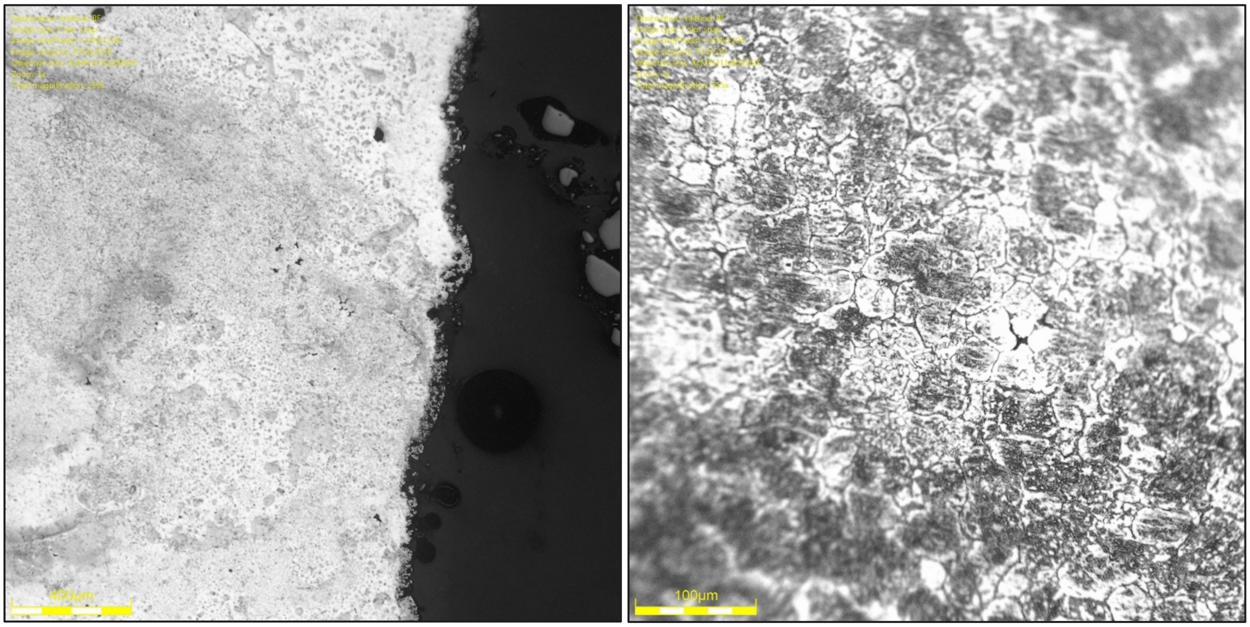

Figure 5.12: U-50Zr #4 Top As-Cast Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

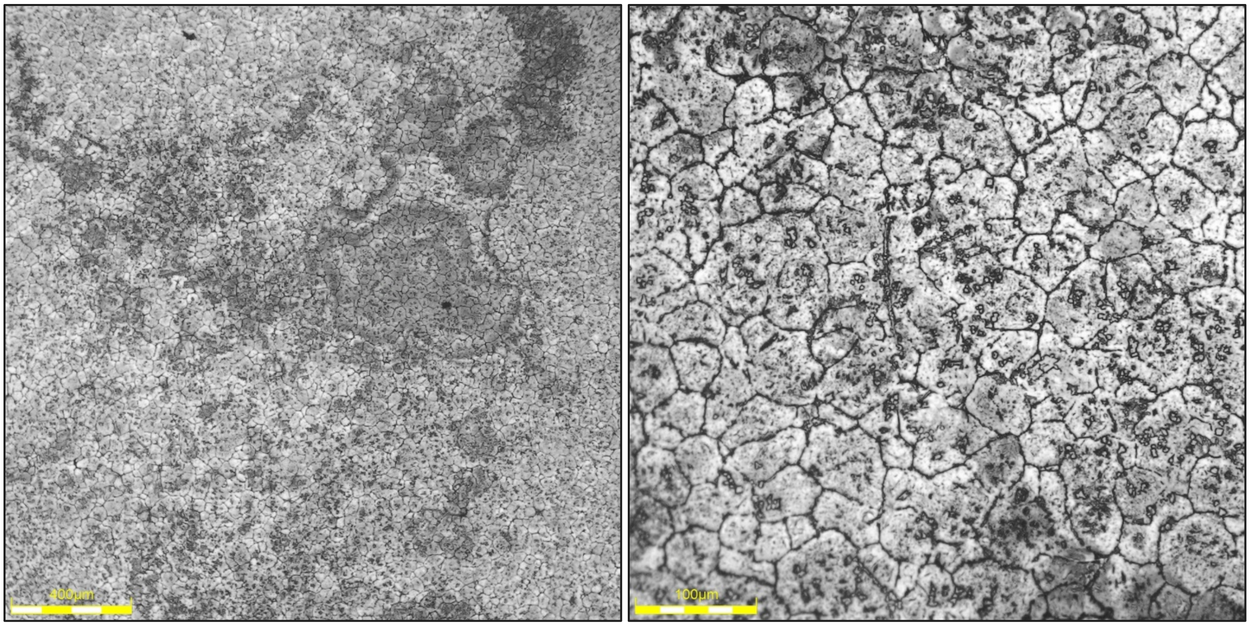

Figure 5.13: U-50Zr #4 Middle As-Cast Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

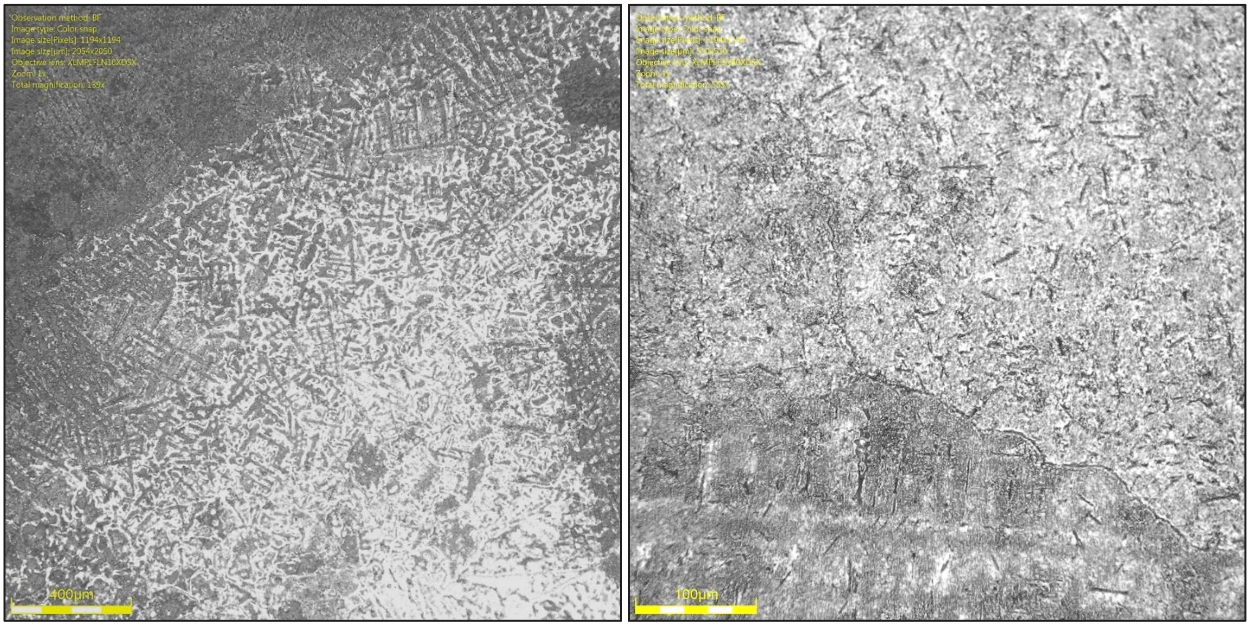

Figure 5.14 U-50Zr Arc Melted Feedstock Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

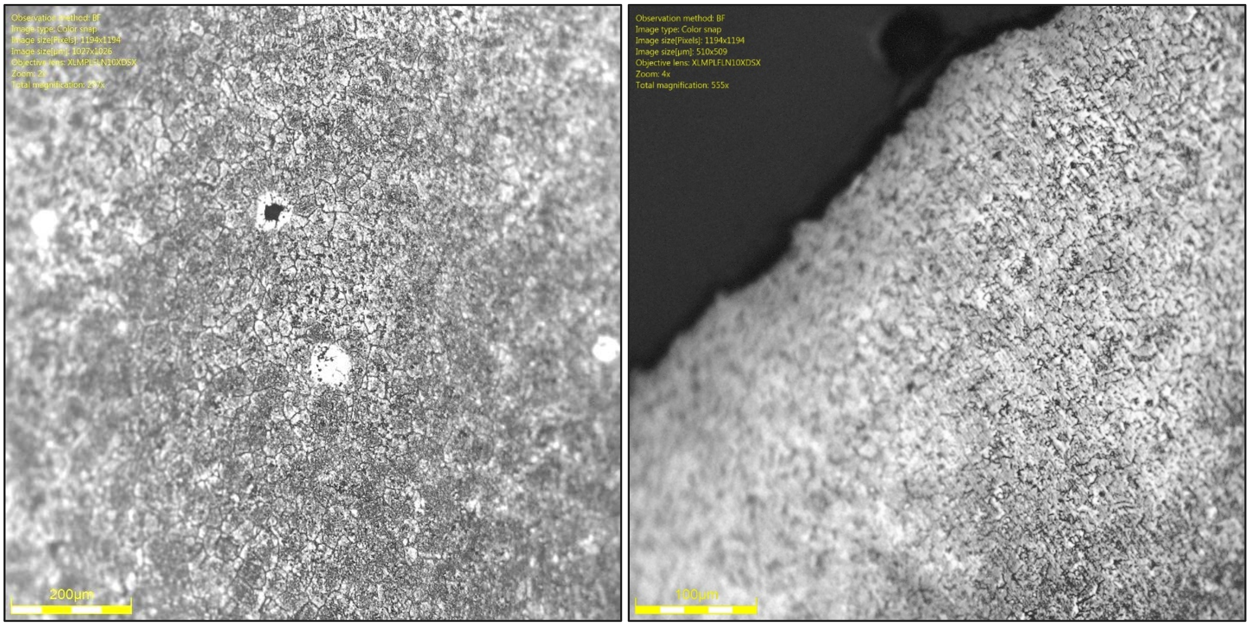

Figure 5.15: U-50Zr #4A Extrudate Micrograph (left: 277x, right: 555x) Scale bar is 200µm and 100µm, respectively

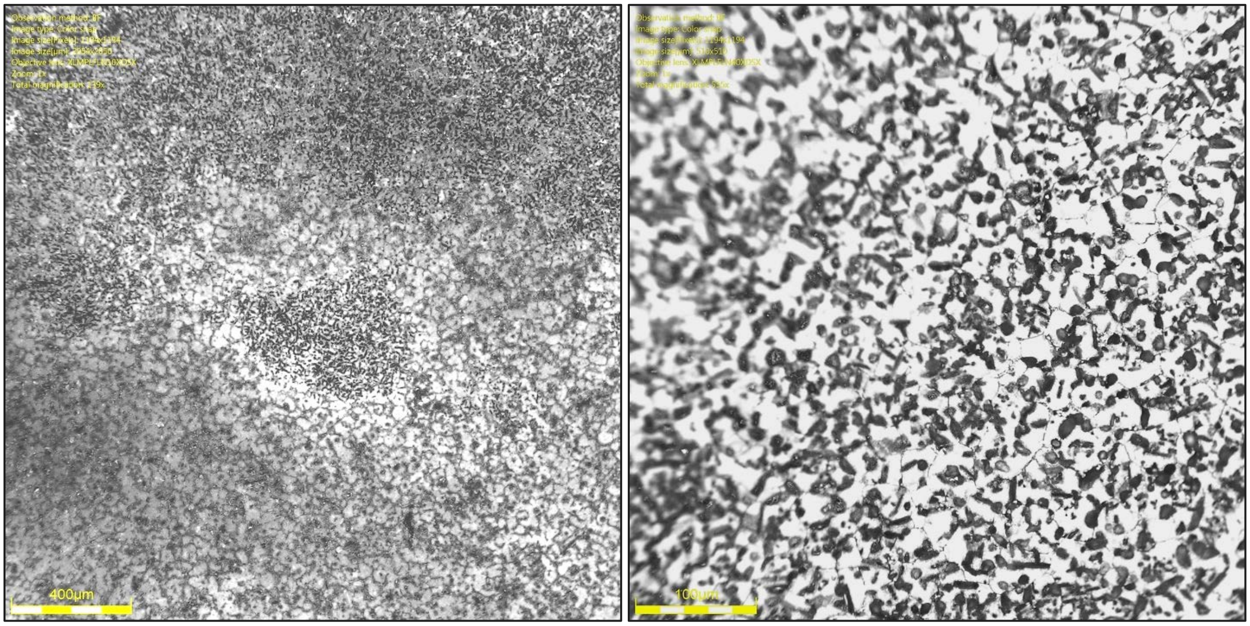

Figure 5.16: U-50Zr #4B Heat Treated Upset Billet 96hr 900°C Micrograph (left: 139x, right: 555x). Scale bar is 400µm and 100µm, respectively

6.0 Discussion

The micrographs for as-cast ingots #1 and #2 U10Zr display unclear phase formation and varied precipitates. The ingot top microstructures appear to display a potential for αU, $\acute{\alpha} U$, αZr, retained γU, and δUZr_2. This coincides with the hypothesized lack of homogeneity as a result of the poor constituent mixing discussed in the casting section of this report. αZr, retained γU, and δUZr_2 are inherent with a saturated zirconium content. This is rational considering the VIM is a tilt-pour system (lower crucible contents potentially form the ingot top) and a significant portion of zirconium was remnant in the bottom of the crucibles post-pour for ingots #1 and #2. The highest concentration of zirconium would be present at the uranium-zirconium interface near the bottom of the crucible. The higher presence of αZr whiskers in the bottom microstructures suggest a higher content of αU (low zirconium solubility) thereby resulting in greater zirconium precipitates. Furthermore, lower density compounds like that of oxides, carbides, and nitrides typically float in low turbulent crucible melts, much like ice in a pitcher of water, resulting in a high concentration of these compounds in the top of ingots. This increases the potential for impurity stabilized zirconium precipitates as shown in Figures 5.1, 5.3, 5.5, and to a lesser extent 5.8.

Martensite transformation is a possible microstructural feature of ingots #1 and #2. Figures 5.1 and 5.3 show some similarities with microstructures for martensite formed in U-rich UZr alloys,[2] and martensite decomposition microstructures of similar elementally U-rich alloys in ASM.[17] However, the quench rate for all ingots in this study was in the 4-10°C/min range with a mold temperature of approximately 350°C and a melt temperature of 1500-1600°C at the time of pour. This is near the lower end of cooling rates described as sufficient for the diffusionless gamma-omega transformation.[11] Furthermore, there is an expectation of significantly lower Zr concentration in the top of ingots #1 and #2 as previously described. The post-heat treatment ingot #1 samples do have a high degree of similarity between the top and bottom microstructures. This suggest that either zirconium content reached near equilibrium through diffusion or decomposition of the martensite phase during the 96-hour 900°C heat treatment. Post-heat treat hardness of ingot #1 does show softening. This suggests a reduction in local zirconium content and/or possible further martensite decomposition. Further analyses like mass spectroscopy for zirconium concentration and x-ray diffraction (XRD) for phase identification on pre and post-heat treatment samples are warranted to discover more.

The as-cast micrographs for U10Zr #3 display a more homogenous representation of a typical U10Zr two phase structure. This also coincides with the expectation that the arc melted feedstock increased the zirconium diffusion within this ingot. The micrograph of the U10Zr arc melted feedstock illustrates the high level of segregation that can occur between these elements. The left image of Figure 5.7 clearly displays zirconium rich and zirconium lean regions. However, in the as-cast ingot, there is a clear δUZr_2 equiaxed primary phase with alpha zirconium secondary phase whiskers. The zirconium rich agglomerates within ingot #3 appear longer and thinner in comparison to ingots #1 and #2. The carbon content within ingot #3 is near double that to ingots #1 and #2. However, this did not appear to increase the size of the zirconium precipitates in the as-cast or heat treated samples. In fact, the size of the secondary phase precipitates in the heat treated samples of ingot #3 are significantly smaller than those present in the samples of ingot #1. Possible explanation for this are that either martensite decomposition did not play as significant of a role in the homogenization of ingot # 3 as that of #1, or that due to arc melting, zirconium diffusion is more advanced in ingot #3 than that of #1, or that the higher carbon content in ingot #3 refined the grain size and reduced precipitate sizes due to closer grain boundaries.

Due to the substantially higher melting point, the U50Zr alloy is a significantly more difficult alloy to fabricate than that of the U10Zr. However, the microstructure of a nominal U50Zr alloy is more straightforward than that of the U10Zr. This is clear in the as-cast U50Zr micrograph. It shows a single phase homogeneous structure of δUZr_2 equiaxed grains. The casting contains over 1000 ppm of carbon. Therefore, the δUZr_2 grains are bounded by significant concentrations of apparent carbides, with some intergranular inclusions present. Limiting the dissolution of carbon within this alloy, given its +1800°C casting temperature, is challenging. Furthermore, due to this high level of carbon, there is likely a grain refining effect in the pre and post-processed U50Zr billets. This may have impacted the #4B extrudate billet with its increased hardness, decreased average grain size, and minimal post-process smearing of the microstructure.

For most UZr applications, +1000 ppm is known as an unacceptable level of carbon. To that end, graphite crucibles are a significant source of carbon in the VIM process. However, graphite is one of the few materials capable of containing hundreds of grams of zirconium at 1800°C and higher temperatures. Inert coatings like Yttria, Erbia, and Zirconia are used to reduce the interactions between the graphite and molten metal. The effectiveness of these coatings is seriously degraded above approximately 1600°C. Another option is ceramic crucibles. They are essentially transparent to the magnetic coupling of the induction coil in the VIM. Therefore, they are attractive for their increased potential to stir the melt resulting in a more homogeneous mixture. Yet, like the inert coatings, ceramics degrade significantly above approximately 1600°C with a strong solvent like that of zirconium metal. Three ceramics, Zirconia, Thoria, and Beryllia, have the potential for use as crucibles with molten U50Zr as they can tolerate the needed temperature and thermal shock when casting this alloy.

This study used Zirconia twice in an attempt to produce a lower carbon ingot. An Yttria oxide coating was applied to the Zirconia crucibles in the same fashion as the prior castings. One attempt loaded a Zirconia crucible with approximately 300 grams of uranium and 300 grams of zirconium rod like the feedstock for ingots #1-#4. The second attempt loaded a Zirconia crucible with approximately 600 grams of arc melted buttons like the feedstock used for ingot #4. Both attempts failed as significant reactions occurred between the charge material and the crucible wall. Therefore, the suitability of Zirconia cannot be confirmed, and Thoria or Beryllia may be a more suitable option.

7.0 Conclusions

This work was focused on two casting processes and two thermomechanical processes for moderate sized (500-1000g) 10% by weight and 50% by weight zirconium UZr alloys. The first casting process relied on only induction mixing within the VIM system thereby eliminating the need for an arc-melting feedstock preparation step. The second casting process used the arc melting process prior for feedstock to the same VIM system. In this study, the induction mixing process alone with a graphite crucible appears insufficient for the fabrication of UZr alloys. Graphite is suitable with the use of master alloy UZr feedstock. There was a moderate increase of approximately 100 ppm of carbon within the U10Zr alloys. However, there was a near 1000 ppm increase of carbon in the U50Zr alloy. This warrants the use of a ceramic crucible for UZr castings near 50wt% zirconium. Zirconia does not appear suitable for UZr castings near 50wt% zirconium. The use of Beryllia or Thoria may be a more suitable option. However, due to the significantly lower liquidus and lower zirconium content, Zirconia crucibles do appear viable for carbon reduction in the U10Zr system.

The two thermomechanical processes studied here were hot extrusion of the U50Zr system and heat treatment in an argon atmosphere. Extrusion of the U50Zr alloy near 680°C appears a viable choice even with +1000 ppm carbon. Extrusion of this system near 630°C does not appear viable unless significant force and tooling strength is available. Furthermore, there appears to be a moderate increase in extrudate hardness vs as-cast. Heat-treatment did reduce the hardness of as-cast alloys in the U10Zr castings as well as resolve some variance in the microstructures. However, at least for the upset U50Zr billet, heat treatment at 900°C for 96hrs did not have a significant impact on hardness or microstructure.

8.0 References

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Pacific Northwest National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354
1-888-375-PNNL (7665)

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