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Density of U-10wt%Zr Materials

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Density of U-10wt%Zr Materials

INTRODUCTION

There is very little information published concerning the density of U-Zr alloys (uranium-rich). The following information presents a portion of what has been published, as well as additional information recorded by Argonne National Laboratory-West while casting U-10Zr fuel for use in the Experimental Breeder Reactor-II. The fuel was injection-cast into ZrO_2-coated quartz molds, quenching the molten fuel alloy very quickly. The fuel was produced to specifications in which mass/weight, diameter, and length of the fuel slugs were all controlled. Density was not controlled.

ANALYSIS OF DENSITY

The density of U-Zr fuel alloys (uranium-rich) has been described as fitting a "rule of mixtures," namely the atomic fractions and the respective densities of uranium and zirconium determined to first order the density of the alloy. If this were solely because of Vegard's Law, then there should be a solubility of zirconium in uranium, or complete immiscibility. In fact, there is very little solubility, and a third phase (UZr_2) consumes the excess zirconium, so it is less obvious that the mixtures of alpha uranium and UZr_2 (δ phase) will also fit a rule of mixtures. One would have to look closely at the various crystal structures to lay out the reasons for this. It could also be that metastable phases in as-cast U-Zr allow for the Vegard's Law interpretation and that subsequent heat treatment may alter this.

Using the rule of mixtures, the density of the U-10 wt% Zr alloys are shown in Table 1.

Table 1. Calculated density of U-10Zr as a function of zirconium weight fraction using published densities for uranium.

			If ρ_U = 18.98 g/cc		If ρ_U = 19.1 g/cc	
10 wt% Zr	U, at. fraction	Zr, at. fraction	Density, g/cc	99% Density, g/cc	Density, g/cc	99% Density, g/cc
+1% Zr	0.76	0.244	15.92	15.76	16.03	15.87
Nominal	0.78	0.225	16.16	15.99	16.27	16.11
-1% Zr	0.79	0.205	16.40	16.24	16.52	16.35

Two values of uranium density are used in the above table. Online references provided a basis with values of 19.1 g/cc[1,2], 19.05 g/cc[3], and between 18.9 and 19.05g/cc.[4] Table 1 also shows what the density would be if the zirconium concentration changed by ±1 wt%. The allowed variation of zirconium in the production of EBR-II driver fuel was ±1.5 wt% Zr. The 99% density is shown to illustrate the potential impact of small defects in the material.

Basak et al[5] looked at the density (as calculated from lattice parameters) of as-cast (VIM melted and cooled in the crucible) U-Zr alloys and found the following:

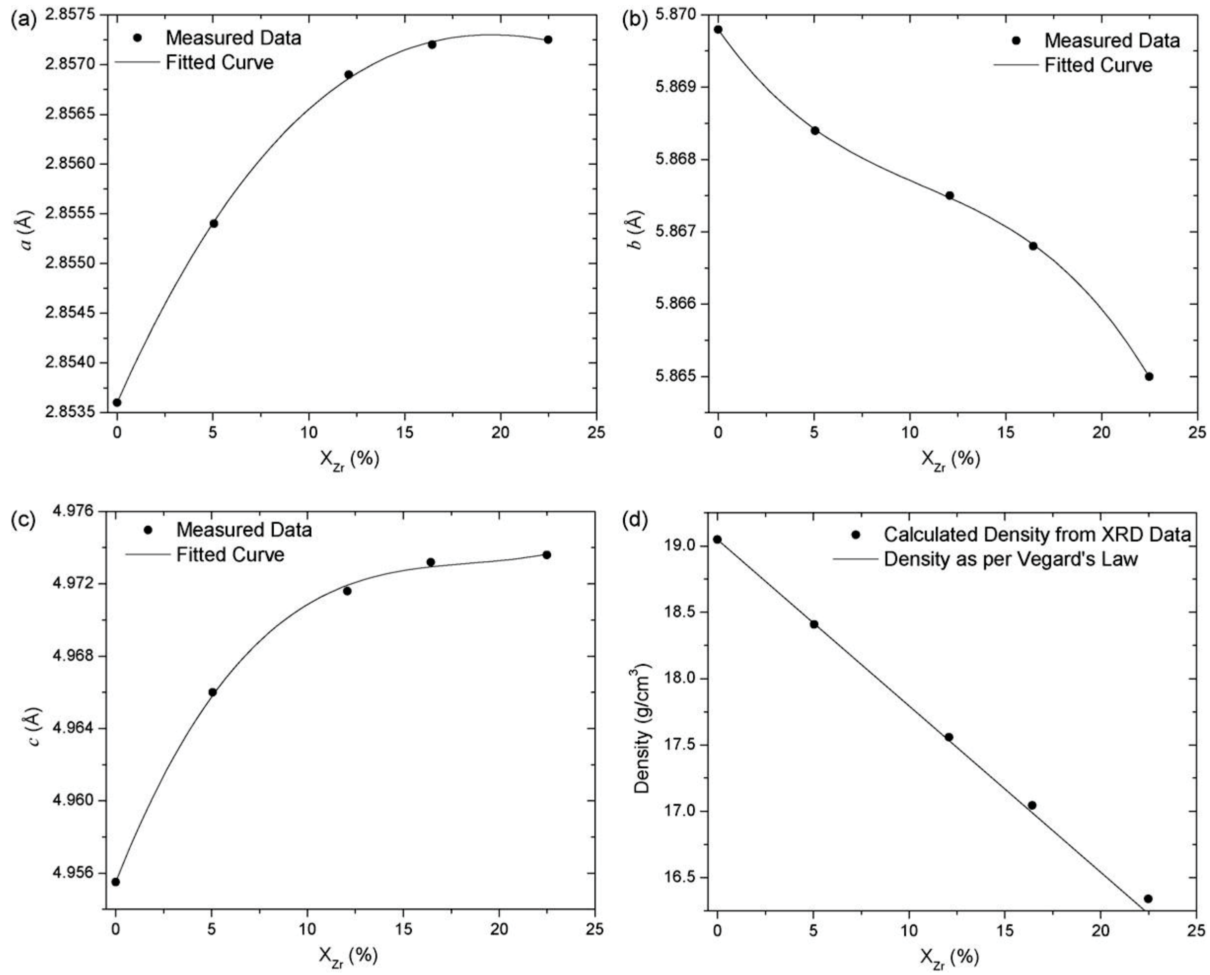

Figure 1. Densities of U-Zr alloys using measured lattice parameters.

The density was calculated from the lattice parameter to see if it fit Vegard's law. It did not, according to the authors. The trend was to deviate to higher density as 10 wt% Zr was approached (see [d]). Note, however, the assumption that no δ phase had formed and that only a supersaturated alpha uranium was present. The related XRD work seemed to support this.

Much earlier, Rough[6] had produced the results shown below in Figure 2. The author did say that several methods were used in producing the data plotted in the figure and noted that there was an adherence to the rule of mixtures. The two stacked points at ~16.0 g/cc are located at the 10 wt% Zr location.

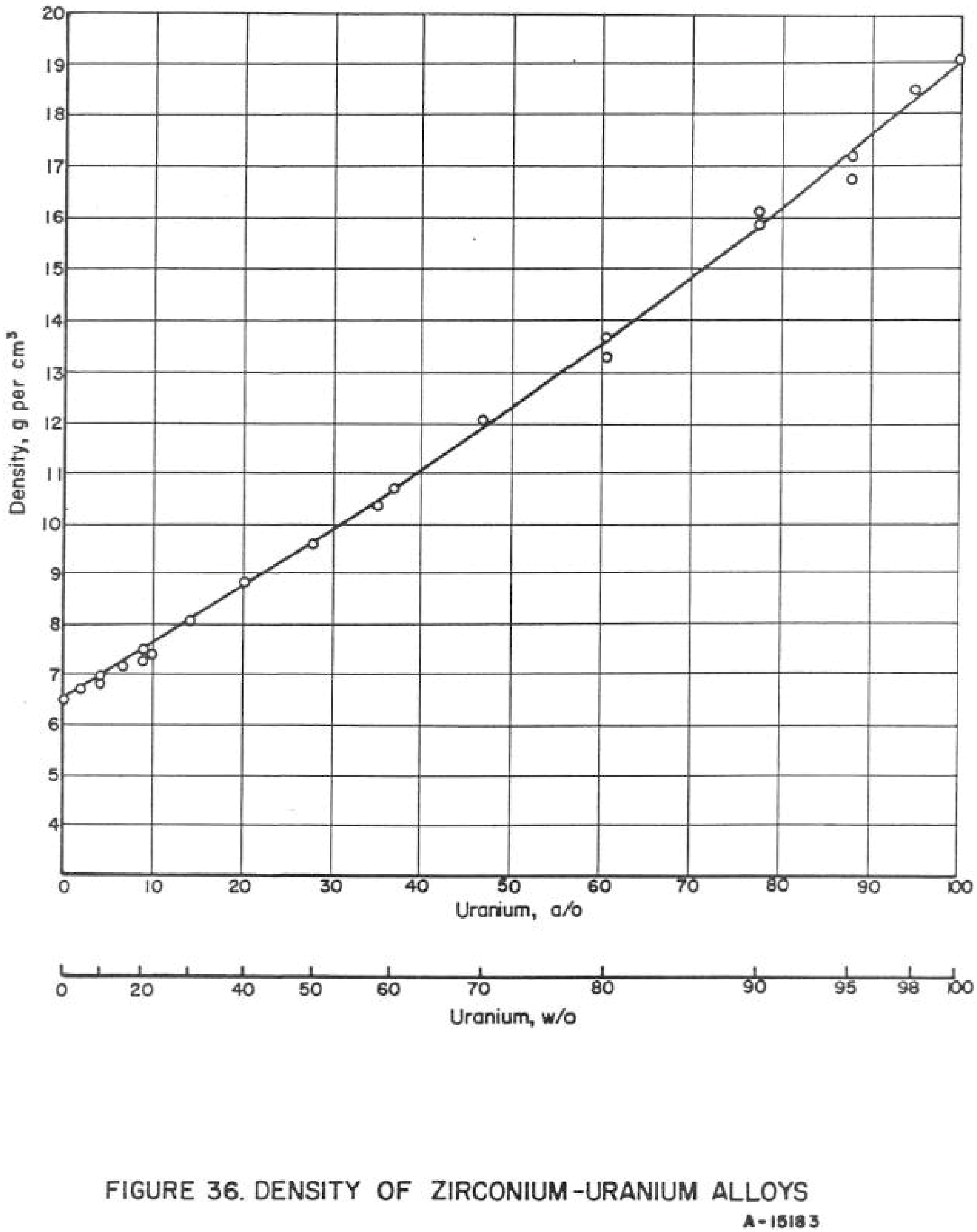

Figure 2. Density of various U-Zr alloys measured using various techniques.[6]

Another source of density data concerning U-10Zr used in EBR-II driver fuel (injection-cast) was from direct measurement of mass and volume. Each cast fuel slug (13.5" long) was measured for length and an average diameter measured at multiple places along the slug length. There were specifications for these dimensions as well as the weight/mass of the slug. Using the mass and dimensions, an apparent density was measured for each slug.

Using this available data for Mk-III (0.173" diameter) and Mk-IV (0.168" diameter) on 492 acceptable fuel slugs, the average density was 15.63 g/cc with a range of 15.11 to 16.06 g/cc. This information can typically be gathered from the fuel slug fabrication packages, the fuel element fabrication packages, or the Experiment Quality Assurance Packages for the specific experiment in which the slugs are used. If used in a standard driver assembly, the information is retrievable from the assembly fabrication package.

Moreover, the mass of the slug often did not correlate well with the density, indicating there are casting defects in these slugs and that they vary in size and number density. To illustrate the nature of the potential defects of the as-cast fuel slugs, Figure 3 shows an example of neutron radiography of an as-cast and bonded (~500°C for ≥1 hour) FFTF-sized fuel pin. The fuel slugs were cast using the same methods and equipment as the EBR-II fuel. Note that the fuel specifications, in terms of allowed diameter, length, and mass would allow densities as low as 14.7 g/cc and as high as 17.1 g/cc. Of course, the latter is not possible if the chemistry meets specification because the rule of mixtures prescribes a maximum density of 8.5 wt% Zr to be ~16.5 g/cc. 14.7 g/cc can be achieved with enough internal defects.

The Figure 3 below shows a radiograph of a section of the fuel column of six pins, two as-cast and the other four following irradiation. The photos were enhanced in brightness and contrast to show the internal defects in the as-cast slugs. It is clear that, even if the fuel itself, without defects, had a density of about 16.0 g/cc as per the rule of mixtures, these fuel slugs with observable defects would have a slightly lower density. Note that the specification is designed only to place a given amount of U-235 evenly distributed in the core. The fuel redistributes itself somewhat due to swelling and zirconium redistribution anyway, so these types of abnormalities cause no problems with fuel or core performance.

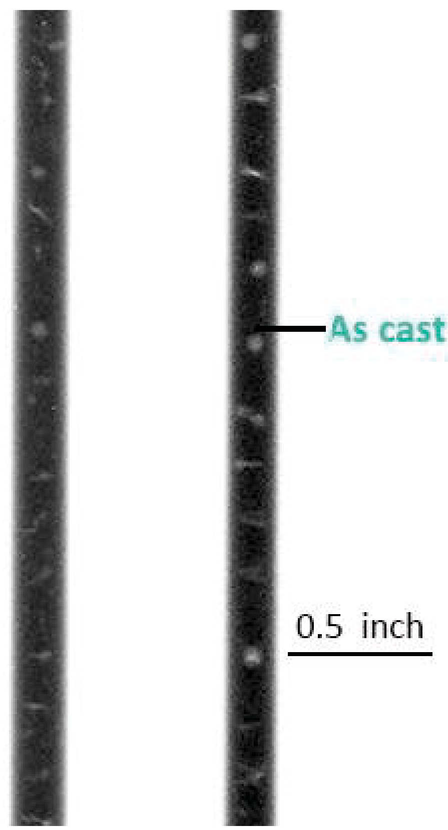

Figure 3. Neutron radiograph of a portion of irradiated and un-irradiated/as-cast FFTF U-10Zr metallic fuel test pins.

Lastly, density was measured at ambient temperature using Archimedes method for water displacement for legacy U-10Zr fuel slugs. Multiple samples were measured at different locations along the fuel slugs. For EBR-II samples, measurements were taken at (insert locations here) of the length of the fuel slug from the spade end, respectively. For FFTF samples, measurements were taken at 95%, 60%, 40% and 5% of the length of the fuel slug, respectively. The calculated results and summary statistics are given in Table 2 and Table 3.

Three fuel slugs, two from an FFTF pin and one from an EBR-II pin[7,8], were taken from a finished, as-fabricated pin, which had undergone a 500˚C, one-hour bonding heat treatment. The slugs were sectioned, and each section was characterized for density using dry and wet/immersion weights, based upon Archimedes Principle.

The EBR-II pin had a single 13.5" fuel slug, while the FFTF pin had two 18" slugs stacked together to form the fuel column. They had been injection cast (rapidly cooled), and inserted into stainless steel cladding with sodium bond. The pins were then bonded at 500°C for approximately one hour.

The sample locations (axially) are listed in Tables 2 and 3. Since there were two stacked slugs in the FFTF fuel column, the "1" and "2" immediately following the "R" indicate which of the two slugs the sample contains. "R" refers to a section taken near axial location a, b, or c. Since the fuel slug could be placed in the cladding with either end of the casting up, that orientation detail was lost. No additional sample preparation other than removal from the mount was necessary.

Table 2. Sample locations for fuel and cladding from EBR-II fuel element.

Region of Interest	Location from the Spade End of Element
Ra (fuel)	1/4 in. to 1 in.
Rb (fuel)	6-3/8 in. to 7-1/8 in.
Rc (fuel)	12-1/2 in. to 13-1/4 in.

Table 3. Sample locations for fuel and cladding from FFTF fuel element.

Region of Interest	Location from the Spade End of Element
R1a (5% of fuel length)	1 ½" to 2 ¼"
R1c (40% of fuel length)	14" to 14 ¾"
R2a (60% of fuel length)	21 ¼" to 22"
R2c (95% of fuel length)	33 7/8" to 34 5/8"

Table 3. Room temperature density of the FFTF U-10Zr fuel slugs.[3]

Sample ID	Location from Spade End, in.	Chemical Composition, wt%	Density (g/mL3)
R2c1 rod end			15.809
R2c	33 7/8 to 34 5/8	90.85U-9.28Zr	15.200
R2a1 rod end			15.448
R2a	21 ¼ to 22	90.85U-9.225Zr	15.850
R2b A			15.497
R2b B			15.591
R1c1 rod end			15.393
R1c	14 to 14 ¾	91.05U-9.205Zr	15.332
R1a1 rod end			15.015
R1a	1 ½ to 2 ¼	91.05U-9.665Zr	15.730
R1b A			15.580
R1b B			14.929
Average			15.448
St. Dev.			0.293
95% CI			0.186

Table 4. Room temperature density of the EBR-II U-10Zr fuel slug.[4]

Sample ID	Location from Spade End, in	Chemical Composition, wt%	Density (g/mL3)
Ra1 rod end			16.165
Ra	1/4 to 1	90.35U-9.78Zr	15.697
Rb	6-3/8 to 7-1/8	90.7U-9.5Zr	15.518
Rb1 rod end			15.546
Rc	12-1/2 to 13-1/4	90.12U-9.83Zr	15.785
Rc1 A rod end			15.557
Rc1 B rod end			15.611
Average			15.700
Standard Deviation (SD)			0.227
95% Confidence Interval (CI)			0.210

Again, the presence of defects in the as-fabricated fuel slugs seems to have produced relatively low density values and variation in density of these samples.

CONCLUSIONS

The density of U-Zr alloys (uranium-rich) has been found to follow the rule of mixtures. That is, the atomic percent of zirconium times the density of zirconium plus the atomic percent of uranium times the density of uranium equals the density of the alloy. The density of U-10 wt% Zr (22.4 at.% Zr) should have a theoretical density of about 16.2 g/cm^3, the absolute value depending on which published value of the density of uranium is correct.

The fuel that was injection cast to fabricate U-10Zr fuel for EBR-II had an average density of 15.6 g/cm^3, lower than the theoretical value. This is not likely influenced by unexpected phase morphology, but more likely due to allowable chemistry variations and an array of small casting defects.

REFERENCES

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[1] Wikipedia

[2] www.rsc.org/periodic-table/elemnt/92/uranium

[3] ead.anl.gov

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