Comparing the Morphology and Solid-State Structure of UTc_3 to URu_3

Nuclear Science & Security Consortium

Josephine Libero, Paula Ramirez, James Louis-Jean Frederic Poineau, Daniel Koury
University of Nevada, Las Vegas

INTRODUCTION

Technetium and ruthenium are high yield fission products from uranium fission that can both be found as part of metallic inclusions in spent nuclear fuel. In ceramic oxide fuels technetium, ruthenium and other light platinum metals are driven into a metallic alloy known as the epsilon phase[1]. These metals can also form metallic species with actinides in nuclear fuel. Bramman et all[2] notes the formations of AnM_3 species (An= U, Pu M=Ru, Rh, Pd) in spent ceramic fuel. These actinide intermetallic compounds are not well characterized in terms of solid-state structure, magnet properties, electronic transport properties, or electronic structure. Understanding the properties of these intermetallic species is important because it can provide data on waste-form behavior and in-reactor fuel behavior.

Furthermore, the fundamental chemistry of Tc is not well understood. By investigating its role in these intermetallic species as a comparison to the chemistry of Ru and Re we can deepen our understanding of complex Tc chemistry. These comparisons will also allow up to build up periodic trend data of how actinides bond with transition metals. In addition, these studies can provide information on the role of 5f electrons in structure, bonding, magnetism, and electron transport properties.

URu_3 is well studied compared to the other species of interest so it is used to verify our methodology. These techniques are then applied all other species. This work will go on to include a variety of AnM alloys (An= Th, U, Np, Pu M= Ru, Re, Tc) in a range of intermetallic compositions

METHODS

- Ammonium pertechnetate was decomposed to TcO_2 in a tube furnace under flowing argon gas at 750°C for 4 hours.
- TcO_2 was reduced to technetium metal powder (Fig 1) in a tube furnace under flowing H5 gas (95% Ar 5% H_2) at 800°C for 4 hours. Tc metal was confirmed using powder x-ray diffraction (PXRD)
- Ru and Tc powder were weighed out in precise ratios to the weight of the U discs and pressed into pellets (d = 6 mm) (Fig 2)
- U discs (d = 6 mm) were cut from a metal U rod and sanded to remove the oxide layer formed in air


Figure 1: Tc metal that was reduced from NH_4TcO_4


Figure 2: Pellet pressed from Ru metal powder


Figure 3: Arc Melter in action


Figure 4: Vacuum sealing of UTc_3 alloy in quartz tube

- A U disc and Tc/Ru pellet were stacked vertically & arced (Fig 3) for 30-seconds, three times total in a half atm of pure argon gas
- Each alloy was vacuum sealed (Fig 4 and 5) into quartz tube that has been back filled with Ar to minimize oxygen content. The UTc_3 alloy was sealed with tantalum to serve as a getter material
- The URu_3 alloy was annealed at 750° C for 10 days and allowed to cool to room temperature naturally and the UTc_3 alloy was annealed at 800°C for 10 days and allowed to cool at a rate of 50°C per 15 minutes


Figure 5: Samples in sealed quartz tube before annealing

- The samples were cut along their equator and polished to 1 micron in order to perform SEM, EDS and PXRD
- Computational studies were done in Quantum Espresso[3,4] using Ultra Soft PBE pseudopotentials. PXRD simulated with VESTA

RESULTS AND DISSCUSION

SEM & EDS of URu_3

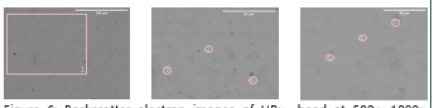
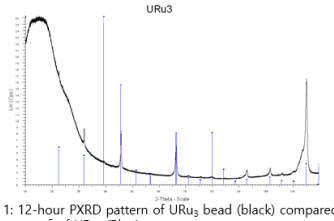


Figure 6: Backscatter electron images of URu_3 bead at 500x, 1000x, and 2000x magnification. Areas/Points for EDS quantification shown

	1	2	3	4	5	6	7
Uranium	24.04	25.29	66.24	23.63	26.70	25.54	25.39
Ruthenium	75.96	74.71	33.76	76.37	73.30	74.46	74.61

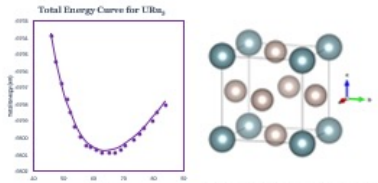
Table 1: Results of EDS quantification of URu_3 in atomic precent

PXRD of URu_3



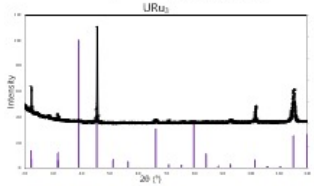
Graph 1: 12-hour PXRD pattern of URu_3 bead (black) compared to known pattern[5] of URu_3 (Blue)

DFT of URu_3



Graph 2: Total energy as a function of volume for URu_3

Figure 7: Structure of URu_3 with optimized lattice parameters from total energy curve



Graph 3: 4-hour pattern of URu_3 (Black) compared to PXRD pattern of optimized structure simulated in VESTA (Purple)

RESULTS AND DISCUSSION

SEM & EDS of UTc_3

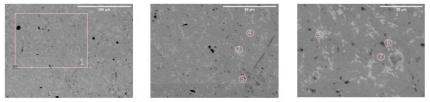
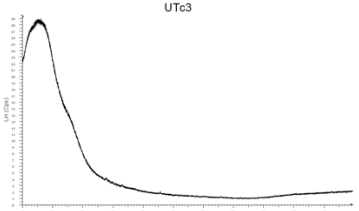


Figure 8: Backscatter electron images of UTc_3 bead at 250x, 1000x, and 2000x magnification. Areas/Points for EDS quantification shown

	1	2	3	4	5	6	7
Uranium	25.44	33.05	23.30	23.45	32.73	22.49	23.02
Technetium	74.56	66.95	76.70	76.55	67.27	77.51	76.98

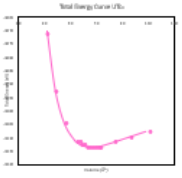
Table 2: Results of EDS quantification of UTc_3 in atomic precent

PXRD of UTc_3



Graph 4: 12-hour PXRD pattern of UTc_3 bead (black)

DFT of UTc_3


Graph 5: Total energy as a function of volume for UTc_3

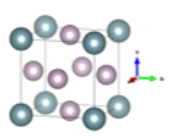
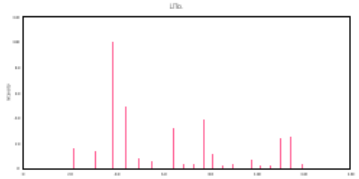


Figure 9: Structure of UTc_3 with optimized lattice parameters from total energy curve


Graph 6: PXRD pattern of optimized structure simulated in VESTA (Pink)

CONCLUSIONS

UTc_3 is forming multiple phases throughout the sample, primarily UTc_3 and UTc_2.
This suggests URu_3 either has a lower melting point, so it was more effectively annealed at 800°C and/or that URu_3 is a more energetically favorable state than UTc_3.
Insufficient annealing temperature explains the lack of crystallinity in the UTc_3 sample.
UTc_3 needs to be annealed again at a higher temperature

FUTURE WORK

Reannealing UTc_3 alloy and do SEM, EDS, and PXRD again
Synthesize and Characterize other compositions of uranium-ruthenium and uranium-technetium alloys from the U-Ru phase diagram
Electron Probe Micro-Analysis (EPMA) and Electron Backscatter Diffraction (EBSD)

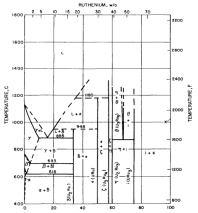


Figure 10: U-Ru Phase Diagram[6]

Physical Properties Measurements including heat capacity, capacitance and magnetic susceptibility
Melting Point Determination and Phase transformations with TGA-DSC

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