INL/MIS-22-69892-Revision-0

Uranium Zirconium Alloy Dissolution

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Doug Porter

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Analytical Laboratory Special Instructions

MFC-AL-SI-22-019

Title: **Uranium Zirconium Alloy Dissolution** LI #: ARL-5000-NOP-002

Sample Description: Dissolution of Uranium Zirconium (with Zr between 5 to 50 wt %) Alloy Samples

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Type of confinement: (Place A ☒ Where Applicable)

☒ Hood ☒ Glovebox ☒ Hot Cells ☐ Glovebag ☐ No Controls (Bench Top/Tray)

(*Requires NFM and Rad Con Engineer approval*)

Type of gloves needed for reagent used: (Place a ☒ where applicable)

☒ Nitrile ☐ PVC ☐ Rubber ☒ Neoprene ☐ Other (As Defined Below)

PURPOSE:

This Special Instructions provides a standard method to dissolve irradiated or unirradiated UZr alloys. The scope of this procedure was developed to facilitate total dissolution of UZ solid samples with and without cladding materials.

Discussion:

Uranium metal alloys are commonly used to provide corrosion resistance for metallic fuels. The use of Zirconium is common in fuel fabrication and the dissolution of these materials is necessary to determine fuel composition and levels of trace impurities. The exothermic and kinetically fast reaction of uranium zirconium alloys (from 1% to 50% Zr) with nitric acid has been well documented. This is due to a reaction between finely divided epsilon UZr phase in a matrix of alpha-uranium with nitric acid. The alpha phase quickly dissolves, leaving small solid particles of Uranium and Zirconium which can explosively react with nitric acid. This is mitigated through the addition of HF which complexes the oxides and prevents reaction. Once the material has been dissolved and only fluoride precipitates remain, a complete dissolution can be achieved by adding boric acid in at least a molar ratio of 1:4 Boron to Fluoride. The boric acid will preferentially bind the fluoride compared to the uranium or the lanthanides and allow the lanthanides and uranium to be solubilized. The amount of boric acid required is calculated in Note 6 below.

In the instance where samples are received with iron based cladding materials that also need to be concurrently dissolved then an HCl based method for dissolution is preferred. This is performed under section 2 below.

References:

1) R.P. Larsen, R.S. Shor, H.M. Feder, and D.S. Flikkema, "A Study of the explosive properties of Uranium Zirconium Alloys," Argonne National Laboratory, Chemical Engineering Division, ANL-5135 July 1954.

2) R.P Larsen, "Dissolution of Uranium Metal and its Alloys," Anal. Chem., 31(1956) 545.

3) B.S. Covino Jr., J.V. Scalera, T.J. Driscoll, J.P. Carter. "Dissolution Behavior of 304 Stainless Steel in HNO3/HF Mixtures". 1986, Metallurgical Transactions A, 17A, 137-149. https://doi.org/10.1007/BF02644450.

4) C.J. Maher. "Current Headend Technologies and Future Developments in Reprocessing of Spent Nuclear Fuels". 2015, Reprocess and Recycling of Spent Nuclear Fuel, Ch 5, 93-124. https://doi.org/10.1016/B978-1-78242-212-9.00005-8.

5) B.S. Covino Jr., J.V. Scalera, P.M. Fabis. "Pickling of Stainless Steel-A Review". 1984, Bureau of Mines, IC-8985.

Analytical laboratory(s) to be used:

A chemical fume hood may be used **IF** the dose rate **AND** internal exposure rates are within the limits of the appropriate RWP. See LWP-15031, Radiological Control Confinement/Containment Determination, for instructions on the determination of confinement to be used.

Special tools/equipment/supplies/parts to be used:

Balance, Polypropylene Bottles, Tare Boat, PFA Erlenmeyer Flask or other poly-flouro Inert Beakers

Reagents to be used:

NOTE 2: Reagent quality will be determined by trained and qualified personnel, concentrations listed are nominal values for reference.

NOTE 3: Research Point of Contact or SI Author can direct efforts to achieve a suitable dissolution within the boundaries of the Laboratory Instruction.

ASTM Type-1 water, or equivalent.

12 M HCl

24 M HF

16 M HNO_3

4 % Boric acid (w,w) or 2 M Aluminum Nitrate

Specific instructions:

NOTE 4: Perform a process blank along with the samples.

NOTE 5: Irradiated samples are known to be shipped containing finely dispersible solids and care should be taken to limit loss and contamination concerns. When weighing and transferring solid samples an aluminum catch/laydown provides additional contamination control.

1. HNO_3/HF Dissolution Method
   a. OBTAIN tare weight of sample container.
   b. TRANSFER sample into tared container.
   c. OBTAIN an "As Received" sample weight.
   d. As directed by Research point of contact, CLEAN sample by etching in 2 M HF for ≤ 30 seconds, followed by 2 water rinses.
   e. PLACE sample on a clean surface to air dry for at least 30 minutes.
   f. OBTAIN a "Cleaned" sample weight.
   g. TRANSFER weighed sample into a PTFE container.
   h. COVER with ASTM Type-1 water or equivalent.

NOTE 6: Concentrated HF can vary in molarity, which in turn effects the calculations below. IF the concentration of HF is different than 28 M, THEN correct the ratio in line 3 (1 mL / XX mmol) to reflect the actual concentration from the certificate of analysis.

WARNING

First aid must be administered within seconds of exposure to hydrofluoric acid. Hydrofluoric acid in both liquid or vapor state is an extremely toxic corrosive irritant to the skin, eyes, and mucous membranes. Hydrofluoric acid binds with calcium in the body and can penetrate into underlying tissue with serious health consequences. Liquid contact with skin and eyes produces severe and painful burns and immediate blindness.

1) (_____g Zr) x (66 mmoles HF/g Zr) = _____ mmoles HF (minimum)
2) (_____mmoles HF) (minimum) * 1.5 = _____mmole HF (required)
3) (_____mmoles HF) (required) * 1 mL/ 28 mmol HF) = _____ mL of M HF (required)

i. ADD 25 mL of 8 M HNO_3 (containing excess HF based on the Zr content, see NOTE 5 above) per gram of sample.
j. WAIT for reaction to proceed to completion at ambient temperature.
k. PLACE sample on hot plate.
l. When reaction rate has slowed, REMOVE the sample from the hotplate AND allow sample to cool.

Caution

A significant amount of gas formation may occur when adding concentrated hydrochloric acid solution to a hot nitric acid solution. Ensure that the sample has had significant time to cool before proceeding

m. Slowly, ADD 3 mL 12 M HCl
n. RETURN the sample on hot plate.
o. MAINTAIN the solution volume with 8 M HNO_3.

NOTE 7: A qualitative determination for the presence of chloride in a solution can be performed by the visual yellow color of the dissolver blank solution.

p. HEAT the solution until chloride is removed.
q. REDUCE the sample volume to 15 mL.
r. REMOVE the sample from the hotplate AND allow sample to cool.
s. Quantitatively TRANSFER sample to dissolver bottle.
t. DILUTE solution to 50 mL with 2 M HNO_3.
u. OBTAIN stable dissolver solution weight.

2. HCl Dissolution Method
a. Obtain a tare weight for the Erlenmeyer Flask, or screw cap container.
b. TRANSFER the sample to the Erlenmeyer Flask
c. OBTAIN "As received" sample weight,
d. NOTE the condition of the sample
e. COVER the sample with H_2O
f. Carefully ADD 50 mL of 12 M HCl
g. ALLOW the reaction to proceed until reaction slows or ceases at ambient temperature.
h. If Necessary OR under direction of the Research POC, ADD a sufficient amount of HF to prevent formation of ZrO_2.
i. PLACE sample(s) on hotplate.
j. HEAT the sample(s) until solution is refluxing.
k. MAINTAIN volume using 6 M HCl.
l. REMOVE sample from hotplate when reaction is no longer proceeding.
m. IF residues remain in solution
THEN Slowly ADD 10 mL 16 M HNO3 and heat the solution
ELSE PROCEED to Step 2.r
n. ALLOW sample to react at ambient temperature until reaction has slowed.
o. PLACE sample(s) on hotplate.

NOTE 8: A qualitative determination for the presence of chloride in a solution can be performed by the visual yellow color of the dissolver blank solution.

p. HEAT sample(s) until aqua regia is destroyed.
q. REMOVE sample from hotplate.
r. ADD 4% Boric Acid to complex residual fluoride
s. HEAT sample(s) until any insoluble fluorides dissolve.
t. REMOVE the sample(s) from the hotplate AND allow to cool.
u. TRANSFER sample to dissolver bottle
v. DILUTE solution to 200 mL and 6 M HCl
w. OBTAIN stable dissolver solution weight

Analytical Laboratory Special Instructions

Submitted by: Beau Ballard Date: 7/6/2022

Approvals:

Research Point of Contact: Beau Ballard Date: 7/06/2022

Rad Con Engineer: Patrick Rielly Per Telecon email Date: 7/06/2022

NFM: Richard Farrar Per Telecon email Date: 7/06/2022

PEER REVIEW (as required): Pamela L Wynnyczuk Date: 7-6-2022

Beau D. Ballard

From: Richard S. Farrar
Sent: Wednesday, July 6, 2022 1:16 PM
To: Beau D. Ballard; Patrick S. Rielly; Pamela L. Wiscaver
Subject: Re: 2022-07-05 MFC-AL-SI-22-00X UXZr Alloy Dissolution

Beau,

I concur

Rich

From: Beau D. Ballard <beau.ballard@inl.gov>
Sent: Wednesday, July 6, 2022 12:43 PM
To: Richard S. Farrar <richard.farrar@inl.gov>; Patrick S. Rielly <patrick.rielly@inl.gov>; Pamela L. Wiscaver <pamela.wiscaver@inl.gov>
Subject: 2022-07-05 MFC-AL-SI-22-00X UXZr Alloy Dissolution

All,

We are trying to issue the most recent version of the UZr alloy dissolution SI. I have included the addition of the HCl dissolver as we often have UZr alloys with Steel cladding materials that we dissolve. The only other changes is the formatting and addition of standard hazard statements and notes to the definition of containment to be used and chemical hazards that are associated with this process.

Please review the attached and sign for concurrence.

Regards,

Beau

Beau D. Ballard

From: Patrick S. Rielly
Sent: Wednesday, July 6, 2022 3:15 PM
To: Beau D. Ballard; Richard S. Farrar; Pamela L. Wiscaver
Subject: RE: 2022-07-05 MFC-AL-SI-22-00X UXZr Alloy Dissolution

Beau,

I have reviewed the attached SI and you can sign for me for the Rad Con Engineer.

Patrick S. Rielly, CHP, MS
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Idaho National Laboratory | 1955 Fremont Ave. | Idaho Falls, ID | 83415

Idaho National Laboratory

From: Beau D. Ballard <beau.ballard@inl.gov>
Sent: Wednesday, July 6, 2022 12:43 PM
To: Richard S. Farrar <richard.farrar@inl.gov>; Patrick S. Rielly <patrick.rielly@inl.gov>; Pamela L. Wiscaver <pamela.wiscaver@inl.gov>
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Beau