

Synthesis and Properties of Metallic Technetium and Technetium-Zirconium Alloys as Transmutation Target and Radioactive waste storage form in the UREX+1 Process

Thomas Hartmann^{1,2}, Frederic Poineau², Kenneth R. Czerwinski²

¹Idaho State University/Idaho National Laboratory, 1776 Science Center Drive, Idaho Falls, ID 83402, USA, hartthom@isu.edu

²Harry Reid Center, University Nevada – Las Vegas, 4505 Maryland Parkway, Las Vegas, NV, USA

Abstract –In the application of UREX+1 process, technetium will be separated together with uranium and iodine within the first process step. After the separation of uranium, technetium and iodine must be immobilized by their incorporation in a suitable waste storage-form. Based on recent activities within the AFCI community, a potential candidate as waste storage form to immobilize technetium is to alloy the metal with excess zirconium. Alloys in the binary Tc-Zr system may act as potential transmutation targets in order to transmute Tc-99 into Ru-100. We are presenting first results in the synthesis of metallic technetium, and the synthesis of equilibrium phases in the binary Tc-Zr system at 1400 °C after arc-melting and isothermal annealing under inert conditions. Samples were analyzed using X-ray powder diffraction, Rietveld analysis, scanning electron microscopy, and electron probe micro-analysis, which allow us to construct the binary Tc-Zr phase diagram for the isothermal section at 1400 °C.

INTRODUCTION

In the AFCI program, the UREX+1 process is proposed as one of the most promising technique to separate TRU (transuranic elements) from LWR spent nuclear fuel. The application of UREX+1 results in a good separation of uranium, technetium and iodine using tributyl phosphate. Technetium-99 will be separated together with uranium and iodine within the first process step. After the separation of uranium, technetium and iodine must be immobilized by their incorporation in a suitable waste storage-form. Based on recent activities within the AFCI community, a potential waste storage candidate to immobilize technetium-99 is to alloy metallic Tc-99 with excess metallic zirconium. Alloying metallic Tc-99 with zirconium has potential advantages in terms of the future reuse of Tc-99 and also allows the transmutation of Tc-99 into the stable isotope Ru-100 to an extent of 20 % or higher. Tc-99 is abundant in a variety of nuclear waste streams and has a long half-life of 2.13 E5 years. Released into the environment, Tc-99 is damaging, traveling up the food chain, and is causing cancer in humans. Due to the mobility of pertechnetate, it is believed, that after the anticipated potential failure of engineered barriers in 10,000 to 100,000 years in geological repositories, Tc-99 will cause long-term exposure problems. To avoid the migration and long-term exposure due to the release of Tc-99 from geological repositories, we propose (1) to stabilize Tc-99 by alloying it with zirconium

and, (2) to transmute Tc-99 into Ru-100 facilitating fast flux or thermal flux reactors. This research will be accompanied by extensive phase constitutional studies on the relevant ternary Tc-Zr-Ru system in order to determine the thermodynamics and the extent of the stable phase regions. We further propose to study the impact of irradiation on the intermetallic equilibrium phases by applying ion- and proton irradiation on TEM-ready coupons. Our attempt is to provide a physical and chemical robust waste-storage form for Tc-99 waste streams which further allows the transmutation of Tc-99 into the stable isotope Ru-100. These proposed studies are addressing the current need for a Tc-99 waste-form and will provide answers for current research activities and the separation of TRU elements by applying the UREX+1 process. At UNLV, in a recent effort, a process was developed to separate Tc-99 from iodine and to recover pure metallic Tc-99 under process conditions similar to UREX+1. However, only few thermodynamic data in the binary metal systems technetium–zirconium and technetium–ruthenium exist, but no data on the ternary Tc-Zr-Ru system exist. Furthermore, there are no data available on the alloy's susceptibility to irradiation damage, and only few data are available on leachability and chemical corrosion of technetium-zirconium alloys under the long-term geological storage conditions as expected.

EXPERIMENTAL

The Tc-99 starting material NH_4TcO_4 was obtained from Los Alamos National Laboratory originally purchased from the Oak Ridge Isotope Office. The compound contained a black impurity necessitating purification prior to use by treatment with an ammonia/hydrogen peroxide solution followed by evaporation to dryness. Tc-99 was precipitated as $(n\text{-Bu}_4\text{N})\text{TcO}_4$ and the precipitate was converted to Tc-99 metal by heating at 800 °C for 5 hours under wet Ar atmosphere [1]. Zirconium powder (95% Zr & Hf) was purchased at Alpha Aesar.

Stoichiometric mixtures of Tc-99 and Zr of 6:1, 2:1, 1:1, 1:2, and 6:1 (at.-%) were ground and blended in an Agate mortar and pressed to pellets with 3 mm in diameter applying about 600 MPa pressure. The pellets (about 100 mg) were fused at least four times under purified Argon using a single-electrode arc melter (Centorr, 5SA). The fused samples were annealed at 1400°C under argon atmosphere in a tubular furnace (Mellen, SD18-3x12H-1Z - 1800°C). Minor weight losses of 1-5 wt.-% were measured after arc-melting and annealing, potentially caused by oxygen impurities and the volatilization of technetium.

X-ray powder diffraction (PANalytical X'pert Pro), electron probe micro-analysis, EPMA, (JEOL JXA 8900R), and scanning electron microscopy, SEM, (JEOL JSM 5610) were used as major analytical tools to qualify and quantify phase content and phase compositions. The X-ray diffraction data were collected on 10-20 mg samples with the addition of silicon as internal standard (SRM 640c) to account for sample displacement and goniometer off-set. The diffracted intensities were collected by an X'Celerator Pelletier-cooled silicon strip detector and the X-ray diffraction pattern were quantified by Rietveld analyzes (Burker AXS, Topas 3.0). To perform microprobe analysis, we used about 100 mg of steam-reformed Tc-metal as EPMA standard for the quantification of Tc-99 in the samples. Tc-standard and samples were vacuum mount, ground, and polished to a mirrored finish (1 micron) using a Struers TegraPol-15.

RESULTS AND DISCUSSION

Sample Tc_6Zr

The sample Tc_6Zr as annealed at 1400°C is single-phased and exhibits an average Tc to Zr ratio of 6.24, and a content of 4-5 at.-% oxygen was measured. Tc_6Zr crystallizes in the alpha-Mn structure type (cubic space group I-43m) and the lattice parameter was refined to $a=9.6104(2)$

Å. Rietveld structure refinement of Tc_6Zr based on the structure data for alpha-Mn [2] was successful and refinement residuals (Rwp) of typically 7.4% could be achieved (Fig. 1).

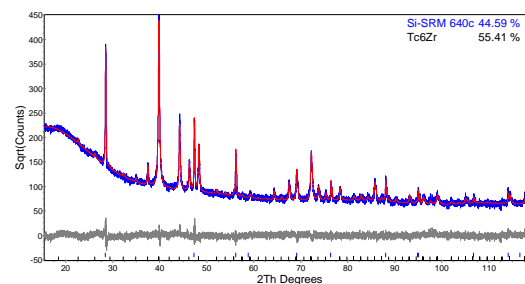


Fig 1. X-ray diffraction pattern of Tc_6Zr , blue: measured; red: calculated; grey: difference.

The atomic coordinates are displayed in Table I and the site occupancies of Tc and Zr confirm the stoichiometry of Tc_6Zr as determined by EPMA, assuming that only the structural 8 c position is occupied by Zr. The shift in stoichiometry to a Tc to Zr ratio of 6.24 might be explained by the partly oxidation and segregation of Zr while arc-melting.

TABLE I. Atomic Coordinates of Tc_6Zr

| Site | Wyckoff letter | x | y | z | B_{eq} |
|------|----------------|-------|-------|-------|-----------------|
| Tc1 | 2 a | 0 | 0 | 0 | 4.6(4) |
| Zr1 | 8 c | 0.318 | 0.318 | 0.318 | 1.6(2) |
| Tc2 | 24 g | 0.357 | 0.357 | 0.357 | 3.0(1) |
| Tc3 | 24 g | 0.090 | 0.090 | 0.282 | 1.8(1) |

Sample Tc_2Zr

Even though a Tc_2Zr phase is reported by Darby et al., [3], fusion and annealing of the Tc_2Zr sample produced the phases Tc_6Zr , Tc_2Zr , and beta-Zr, apparently caused by oxidation of Zr and the subsequent depletion of Zr from the alloy system. This also indicates that the phase stability field for Tc_2Zr at 1400°C might be rather narrow. Electron microscopy revealed Tc_2Zr as the dominant phase (Fig. 2, dark-grey phase) with an average Tc to Zr ratio of 2.04 and an oxygen content of 4 at.-%. Tc_6Zr was determined as minor phase (Fig. 2, light-grey phase) with average Tc to Zr ratio of (only) 4.4 and 3.6 at.-% oxygen impurity. The stoichiometry of the Tc_6Zr -type phase can be explained by a complete substitution of Tc by Zr at the 2 a structural position to allow a rather broad phase stability field of $\text{Tc}_{6.25-x}\text{Zr}$ for $0 < x < 1.45$, increasing the lattice parameter from

$a=9.6104(2)$ Å for $x=0$ to $a=9.751(2)$ Å for $x=1.45$, respectively.

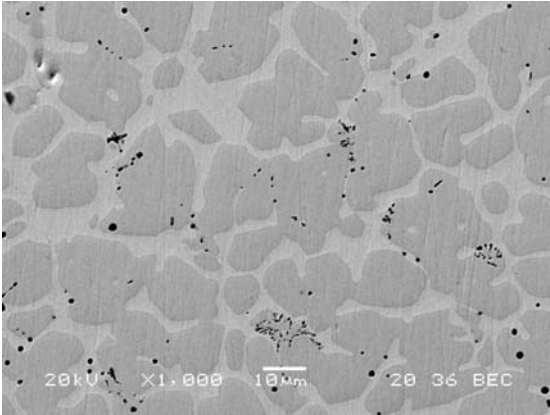


Fig. 2. SEM image of Tc_2Zr using backscattered electrons; Tc_2Zr dark-grey, Tc_6Zr light-grey.

Besides Tc_2Zr and Tc_6Zr , X-ray diffraction combined with Rietveld analysis determined the presence of beta-zirconium (space group $Im\bar{3}m$) in minor quantities (about 0.1 wt.-%) as non-equilibrium phase with a lattice parameter of $a=3.223(1)$ Å to indicate isomorphous substitution of Zr by Tc (Fig. 3).

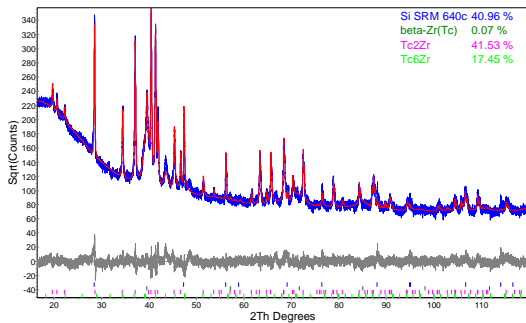


Fig 3. X-ray diffraction pattern of the Tc_2Zr sample, blue: measured; red: calculated; grey: difference; $R_{wp} = 8\%$.

Tc_2Zr crystallizes in the hexagonal space group $P6_3/mmc$. Rietveld analysis could confirm the $MgZn_2$ type structure as reported by Darby et al. [3], and crystallographic parameters are listed in Table II. Zr occupies the 4 f positions of Mg while Tc occupies all 2 a, and 6 h positions of Zn. The lattice parameter could be refined to high precision and a unit cell volume of $203.44(1)$ Å³ confirmed the published data of 204.16 Å³ [3].

TABLE. II: Crystallographic Parameter of Tc_2Zr

| Space Group | | $P6_3/mmc$ (194) | | | |
|--|-------------------|------------------|--------|-------|------------------|
| Lattice Parameter | $a = 5.2160(2)$ Å | | | | |
| | $c = 8.6345(3)$ Å | | | | |
| Refinement Residual for Phase Tc_2Zr | | | | | $R_{wp} = 2.9\%$ |
| Site | Wyckoff letter | x | y | z | B_{eq} |
| Zr1 | 4 f | 1/3 | 2/3 | 0.063 | 3.1 |
| Tc1 | 2 a | 0 | 0 | 0 | 2.5 |
| Tc2 | 6 h | -0.170 | -0.340 | 1/4 | 2.7 |

Sample TcZr

The sample $TcZr$ contains two phases, $TcZr$ as matrix (Fig. 4, grey matrix phase) and Tc_2Zr as minor phase (Fig. 4, light-grey phase). Both phases contain about 5 at.-% oxygen.

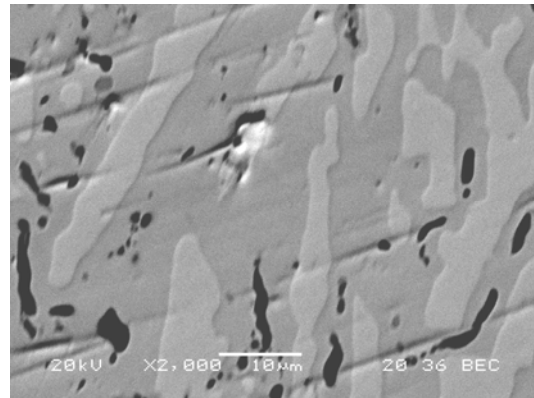


Fig. 4. SEM image of $TcZr$ using backscattered electrons; $TcZr$ grey, Tc_2Zr light-grey.

X-ray diffraction and Rietveld analysis confirm the results by EPMA (Fig. 5).

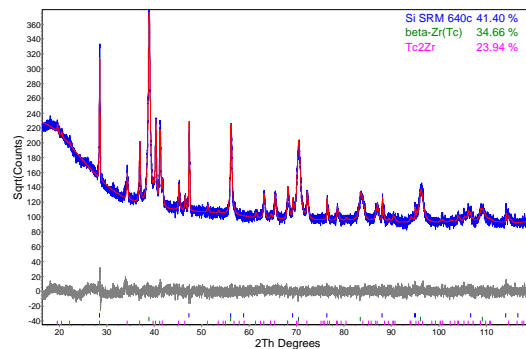


Fig. 5. X-ray diffraction pattern of the $TcZr$ sample, blue: measured; red: calculated; grey: difference, $R_{wp} = 6\%$.

The TcZr phase can be identified as solid-solution-beta-Zr-type phase (cubic space group Im-3m), where 49.8(1) % of the structure sites are occupied by Tc. The lattice parameter of the Im-3m phase ($a=3.2747(5)$ Å) is significantly smaller than the published lattice parameter of pure beta-Zr ($a=3.5453$ Å, PDF 34-657). The Tc₂Zr phase is slightly non-stoichiometric with a Tc to Zr ratio of 1.88(2). The lattice parameter ($a=5.2307(3)$ Å, $c=8.6574(5)$ Å) are slightly larger than the stoichiometric phase (Table II) with no obvious explanation.

Sample TcZr₂

Sample TcZr₂ exhibits an eutectoid micro structure with two phases, an unknown “TcZr₃” phase with a high oxygen content of 18 at.-%, (Fig. 4, dark-grey matrix phase) and a beta-Zr-type solid solution phase Tc₄₈Zr₅₂ (Fig. 4, light-grey phase). The “TcZr₃” phase is poorly crystallized and its structure could not be determined. However, “TcZr₃” is probably a non-equilibrium (low-temperature) Zc(Tc) solid solution phase and a hexagonal P6₃/mmc structure type is assumed.

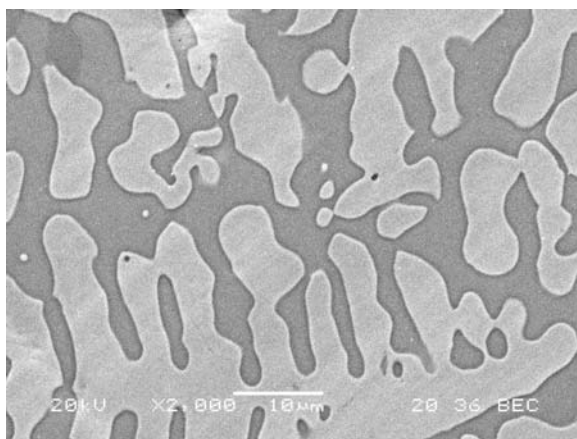


Fig. 6. SEM image of TcZr₂ using backscattered electrons; “TcZr₃” dark-grey, TcZr light-grey.

Sample TcZr₆

The sample TcZr₆ showed partly oxidation of alloyed Zr to Zr₃O (Fig. 7 dark-grey phase). The major binary phase is beta-Zr₇₆Tc₂₄ (cubic space group Im-3m) with a high oxygen content of 13 at.-% (Fig. 7 grey phase). The lattice parameter of beta-Zr₇₆Tc₂₄ ($a= 3.4384(4)$ Å) is significantly larger than the beta-phase in sample TcZr due to its lower Tc content (Fig. 8).

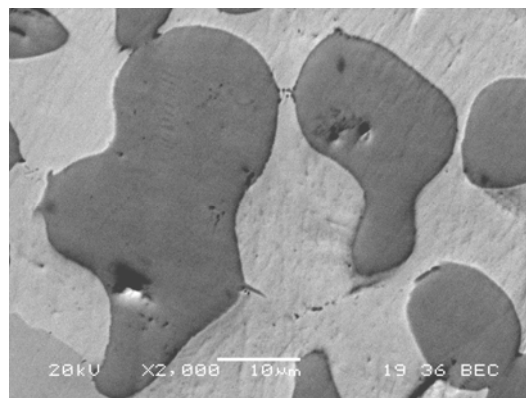


Fig. 7. SEM image of TcZr₆ using backscattered electrons; beta-Zr₇₆Tc₂₄ grey, Zr₃O dark-grey

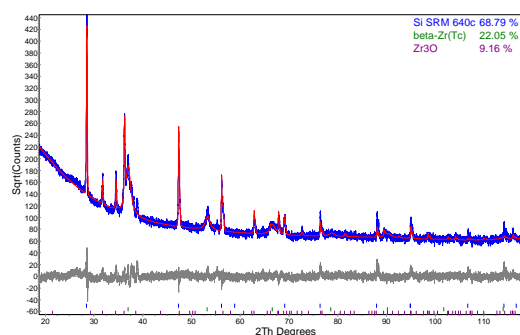


Fig. 8. X-ray diffraction pattern of the TcZr₆ sample, blue: measured; red: calculated; grey: difference, $R_{wp} = 10\%$.

CONCLUSION

- 1) The equilibrium phases in the binary Tc-Zr system could be identified and an isothermal phase-diagram cut at 1400°C can be constructed.
- 2) The stability fields of the intermetallic phases as well as their crystal structures were determined.
- 3) Tc₆Zr might represent the most promising candidate as a Tc host phase or as a transmutation target because of its wide chemical stability field and the simplicity of its fabrication.

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