

## TITANATE WASTEFORMS FOR Tc-99 IMMOBILIZATION

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### ABSTRACT

Technetium is an important radionuclide in nuclear waste management - because of its long half-life and mobility in the environment. In this work technetium has been incorporated into the rutile structure (nominal composition used was  $\text{Tc}_{0.1}\text{Ti}_{0.9}\text{O}_2$ ) by sintering in Ar at 1250, 1300 and 1350°C. At 1300 and 1350°C a significant portion of the Tc inventory was present as Tc metal and there was associated porosity from off-gassing of oxygen. At 1350°C this resulted in large fissures in the sample. Also observed in all samples was a surface layer deficient in Tc that increased in depth from about 40 - 90  $\mu\text{m}$  deep at 1250°C, to ~ 150 - 200  $\mu\text{m}$  at 1300°C, and ~ 250 - 350  $\mu\text{m}$  at 1350°C. This layer is caused by volatilization of  $\text{TcO}_2$  from the rutile accentuated by the fact that the experiments were conducted in flowing Ar. However, all the samples had a core with rutile that was close to the nominal composition, indicating that incorporation of Tc in rutile is viable.

### INTRODUCTION

Technetium-99 has a half-life of  $2.1 \times 10^5$  years, is very mobile in the environment, and has a high biological uptake. For these reasons Tc-99 figures heavily in long-term repository assessments, despite the fact that it is a weak beta-emitter, with a relatively low specific activity compared to many other isotopes. Consequently there is a scientific and political drive to minimize the potential for Tc-99 to leave the repository and a desire to find immobilization solutions to Tc-99-bearing waste streams or to separated Tc-99.

Under oxidizing conditions Tc is heptavalent and is extremely mobile, forming the pertechnetate  $\text{TcO}_4^-$  ion. The higher Tc oxides ( $\text{Tc}_2\text{O}_7$  and  $\text{TcO}_3$ ) are also relatively volatile, so this generally limits the processing conditions to neutral or reducing atmospheres. Under reducing conditions Tc is metallic. In this state it can be encapsulated as sub-micron metal alloy particles inside an inert matrix. For example, high level waste streams which contain Tc can readily be incorporated in synroc-C (a mixture of Ba-hollandite, zirconolite, perovskite and rutile, incorporating ~ 20 wt% high level waste), and consolidated via hot-pressing at ~ 1200°C with a Ti metal buffer. In this waste the Tc is diluted into the metallic alloy particles with Pd, Ru, Rh, Ni and Fe [1], and these in turn are encapsulated by the ceramic phases to give a material with low leach rates. For example, in MCC-1 type tests on the above material in oxidic conditions (open laboratory) at 90°C the Tc leach rates decreased from ~  $10^{-3} \text{ g.m}^{-2}.\text{d}^{-1}$  after ~ 25 days leaching to ~  $10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$  after ~ 100 days [1]. Under anoxic conditions in a glove box ( $\text{P}_{\text{O}_2} < 20 \text{ ppm}$ ) the leach rates were 1000 and 100 times lower, respectively.

For wastes rich in Tc, alternative solutions need to be examined to achieve high waste loadings, the two approaches being encapsulation of the metallic Tc in a durable ceramic matrix or

substitution of  $\text{Tc}^{4+}$  for a lattice ion in a ceramic wastefrom. The  $\text{Tc}^{4+}$  ion has an ionic radius of 0.0645 nm [2] and can partially substitute for  $\text{Ti}^{4+}$  (ionic radius = 0.0605 nm) in titanate ceramics. In previous work at ANSTO attempts have been made to substitute  $\text{Tc}^{4+}$  for  $\text{Ti}^{4+}$  in synroc phases via hot-pressing in graphite dies and hot-isostatic pressing in stainless steel bellows/cans with Ti, Fe and Ni buffers [1, 3-5]. In many cases the conditions in the can or die were too reducing and Tc metal formed. It was found that alloying with Fe and Ni to produce a “stainless steel” was required to prevent high initial Tc leach losses, as the Tc metal on its own was not durable enough and easily oxidized after only a few days to form the soluble pertechnetate ion. A perovskite sample of  $\text{CaTc}_{0.5}\text{Ti}_{0.5}\text{O}_3$  stoichiometry was made via hot-pressing at 900°C in graphite followed by sintering at 1500°C in Ar. In this sample the volatile losses were ~ 20 % of the Tc [1,5]. The phases formed on hot-pressing were perovskite  $\text{CaTc}_{0.1}\text{Ti}_{0.9}\text{O}_3$ , CaO, plus Tc-metal. Upon sintering at 1500°C the material formed single-phase perovskite with the composition measured being  $\text{CaTc}_{0.42}\text{Ti}_{0.58}\text{O}_3$ .

Perovskite ( $\text{CaTiO}_3$ ) and spinel ( $\text{Mg}_2\text{TiO}_4$ ) were suggested as matrices at Pennsylvania State University in the 1980s [6,7], work which followed on from earlier crystallographic research on Tc-oxides [8]. Apatite has also been proposed as a wastefrom for Tc [9]. Some workers have looked at the incorporation of Tc in stainless steel [10,11]. Keiser, et al. looked at immobilizing Tc in stainless steel alloys, similar to synroc-C work above [4,5]. They were able to incorporate 2 wt% technetium into a stainless steel - 15 wt% zirconium alloy [10]. No Tc-rich phases were detected, with the Tc being distributed amongst the stainless steel phases.

Other matrices tested for Tc immobilization include cement grouts either for direct immobilization or the immobilization of Tc-loaded ion exchange resins [12-15]. These cements were found to be more effective when blast furnace slag was added, which was believed to reduce the pertechnetate ion to the less soluble  $\text{Tc(IV)}$  ion. Phosphate-bonded cements, magnesium potassium phosphate, have also been proposed [16], but only for dilute amounts of several hundred ppm of Tc. Technetium is partially incorporated into borosilicate glass as part of the HLW immobilization process, but volatility losses in the melter under oxidising conditions remain a problem particularly above ~ 500-550°C [17-19]. Reducing conditions can lead to segregation of the  $\text{TcO}_2$  or Tc metal in the glass [16]. However, recently plant data from the DWFP facility at Savannah River has led to claims that a melter cold-cap could reduce Tc volatility [19], although this waste stream was pretreated with formic acid, which reduces the  $\text{Tc}^{7+}$  to  $\text{Tc}^{4+}$  [18,19].

In the current work we discuss the results of some sintering trials carried out on substituting  $\text{Tc}^{4+}$  into the  $\text{Ti}^{4+}$  site of rutile. The aim was to see if these simple solid-state sintering techniques could be used to make Tc-doped rutile. Sintering routes would be relatively easy to implement in a radioactive plant using existing technology. Attempts have previously been made to fabricate Tc-doped rutile ( $\text{Ti}_{0.67}\text{Tc}_{0.33}\text{O}_2$ ) via hot pressing in stainless steel bellows in graphite dies at 1200°C. When Fe/FeO buffers were used all the Tc was reduced to metal. A coarse NiO buffer resulted in partial incorporation of Tc in rutile but Tc metal still formed [1].

## EXPERIMENTAL

Tc-doped samples were prepared via wet-mixing of the Tc, added as ammonium pertechnate,  $\text{NH}_4\text{TcO}_4$ , with anatase powder and drying the slurry on a hot plate. The dried cake was calcined in Ar at  $500^\circ\text{C}$  (previous work showed that the volatile Tc losses were low in alkoxide-precursor systems [4]). The calcined powder was then ground in a mortar and pestle. Pellets were prepared from the powder via cold-pressing into disks of 10 mm diameter and sintering these disks in an alumina tube furnace on Pt foil at 1250, 1300 and  $1350^\circ\text{C}$  in flowing argon ( $\sim 0.3$  l/min.) for 8 hours. Heating and cooling rates were  $5^\circ\text{C}/\text{min}$ .

Samples were examined by theta/2 theta x-ray diffraction (XRD), using a Siemens D500 instrument with Co K-alpha radiation or a Scintag X1 machine utilizing Cu K-alpha radiation. XRD was carried out on solid disks of the sample that had been polished flat. Scanning electron microscopy (SEM) was carried out using a JEOL JSM6300 unit fitted with Noran energy dispersive x-ray spectroscopy (EDS) systems for chemical analysis. Particle size analysis was carried out by the laser light diffraction method using a Malvern Mastersizer MS2000.

## RESULTS AND DISCUSSIONS

Sintering the Tiona AG anatase powder alone indicated that the powder sintered to  $\sim 92 - 93$  % theoretical density by  $1250^\circ\text{C}$  and to between  $\sim 93.5$  and  $97$  % by  $1500^\circ\text{C}$ . To reduce the risk of Tc metal formation and volatilization it was decided to sinter at the lower temperatures of 1250, 1300 and  $1350^\circ\text{C}$ , where adequate density pellets should be feasible.

XRD analysis of the three sintered  $\text{Tc}_{0.1}\text{Ti}_{0.9}\text{O}_2$  samples ( $1250$ ,  $1300$  and  $1350^\circ\text{C}$ ), indicated that the main phase in all samples was rutile. Tc metal was only detected in the  $1350^\circ\text{C}$  sample. However, XRD can prove to be unreliable when looking for small amounts of secondary phases, hence the need to conduct SEM analysis.

At  $1250^\circ\text{C}$  the sample was composed only of rutile (Fig. 1). Tc metal was not detected. The surface layer of the pellet was more porous and deficient in Tc relative to the target composition to a depth of  $\sim 40 - 90$   $\mu\text{m}$  (Fig. 1). The composition of this layer as measured by EDS analysis was  $\text{Tc}_{0.055}\text{Ti}_{0.945}\text{O}_2$ . Some regions of residual  $\text{TiO}_2$  agglomerates, deficient in Tc, were present in the bulk of the sample (Fig. 1a). The Tc-deficient regions are a residue of the original agglomerates in the  $\text{TiO}_2$  raw material that have not been broken up during grinding. The median particle size of the Tiona AG raw material has been measured at  $\sim 2.5$   $\mu\text{m}$  and the distribution suggests that the particles are between  $1 - 2$   $\mu\text{m}$  with some agglomerates of  $\sim 10 - 50$   $\mu\text{m}$ . More intense mixing can eliminate these agglomerates, e.g., ball milling; the samples here were only ground in a mortar and pestle. Also present were some regions relatively rich in Tc, which are seen as lighter contrast areas in the SEM backscatter electron images (Fig. 1). EDS analysis of one of these Tc-rich regions (Fig. 1b) gave a composition of  $\text{Tc}_{0.19}\text{Ti}_{0.81}\text{O}_2$  compared to the surrounding matrix composition of  $\text{Tc}_{0.07}\text{Ti}_{0.93}\text{O}_2$  (Fig. 1b).

The  $1300^\circ\text{C}$  sintered sample is mainly rutile though it also contains Tc metal ( $\sim 5 - 10$  vol. %) and associated porosity (Fig. 2). The centre of the pellet had a measured EDS composition of  $\text{Tc}_{0.09}\text{Ti}_{0.91}\text{O}_2$ , which is close to that of the target composition. As with the  $1250^\circ\text{C}$  sample,

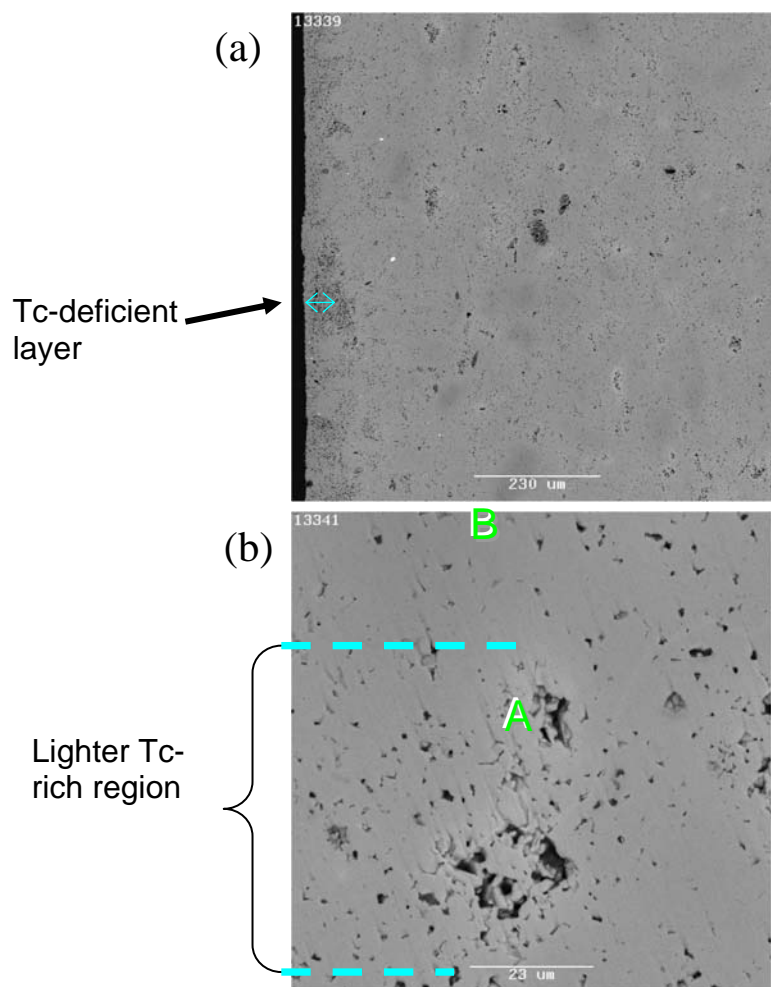


Fig. 1 SEM Backscatter Electron Micrograph of the sample fired at 1250°C, ar, 8 hours. (a) 100x, the residual effects of agglomeration can be seen between the darker tc-deficient and lighter and more porous tc-rich regions. The surface of the pellet is more porous and is slightly deficient in tc. (b) 1000x around pores with a lighter contrast tc-rich region (a,  $\text{tc}_{0.19}\text{ti}_{0.81}\text{O}_2$ ) compared to the surrounding matrix (b,  $\text{tc}_{0.07}\text{ti}_{0.93}\text{O}_2$ ). bright spots in (a) are a refractory contaminant from the mortar and pestle.

regions that were deficient in Tc ( $\text{Tc}_{0.03}\text{Ti}_{0.97}\text{O}_2$ ) from residual  $\text{TiO}_2$  agglomerates were still present in the 1300°C sample (Fig. 2a). The exterior of the pellet was again deficient in Tc to a depth of ~ 150 - 200 μm (Fig. 2b), with the layer composition ~  $\text{Tc}_{0.02}\text{Ti}_{0.98}\text{O}_2$ .

The test sample sintered at 1350°C had extensive Tc metal formation and was very porous with what appears to be large fissures in the pellet (Figs. 3 and 4), indicative of gas formation within the samples. As mentioned above, equivalent Tc-free samples were quite dense. The surface has a layer deficient in Tc and this layer is deeper, ~ 250 - 350 μm (Fig. 4a), than the 1250 and 1300°C samples. The composition of this layer was similar to that of the 1300°C layer (~  $\text{Tc}_{0.02}\text{Ti}_{0.98}\text{O}_2$ ). In the bulk of the material the rutile composition away from the Tc metal was that of the

target composition  $Tc_{0.1}Ti_{0.9}O_2$  (Fig. 4b). Next to the Tc metal particles the composition was somewhat deficient in Tc ( $Tc_{0.07}Ti_{0.93}O_2$  {Fig. 4d}).

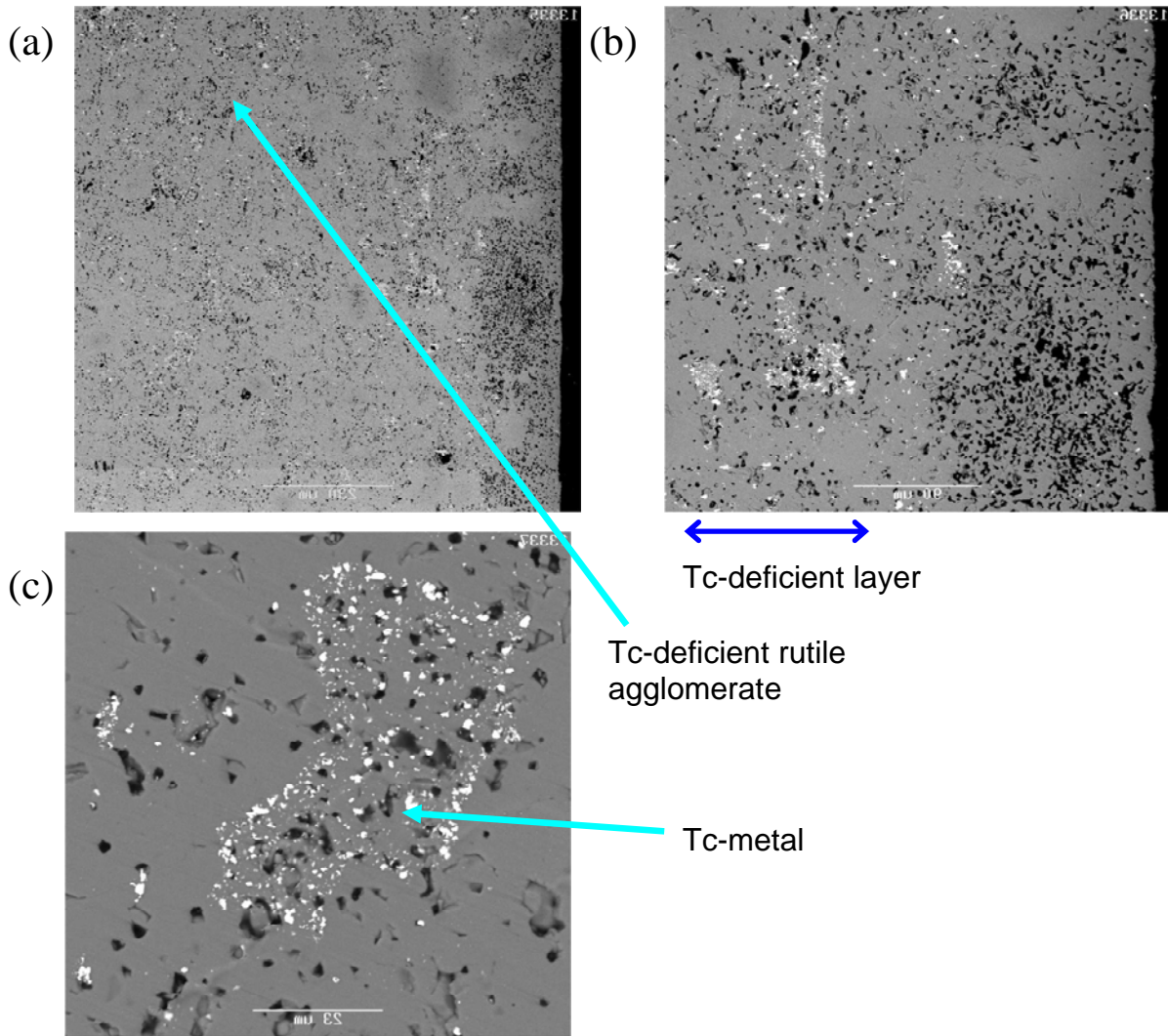


Fig. 2 SEM backscatter electron micrograph of the sample fired at 1300°C, Ar, 8 hours. (a) 100X, (b) 250X and (c) 1000X. Tc metal (light spots) can be seen throughout the sample. The surface of the pellet is porous and deficient in Tc.

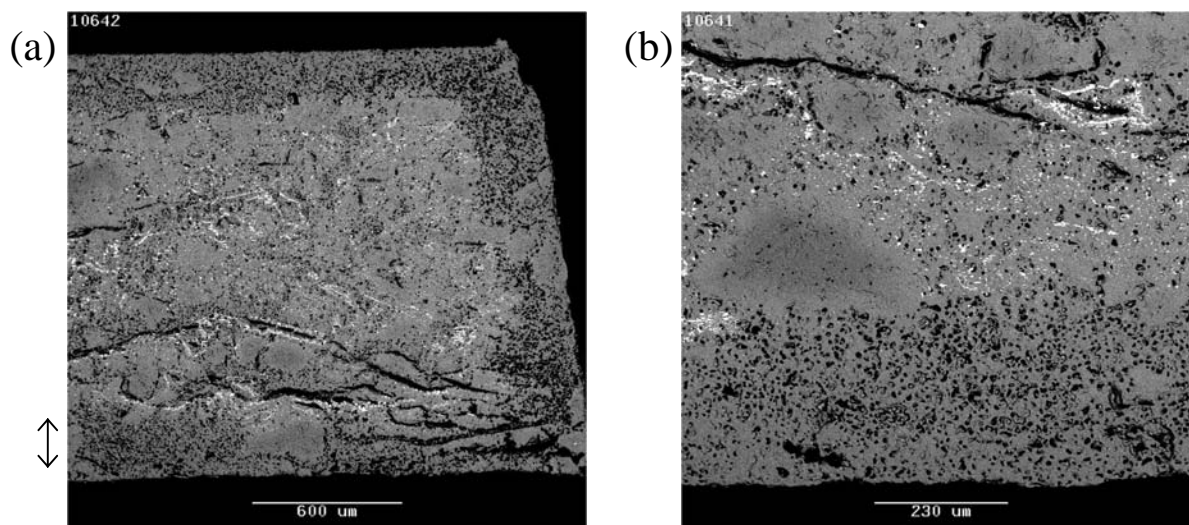


Fig. 3 SEM backscatter electron micrograph of the sample fired at 1350°C, Ar, 8 hours. (a) 43X and (b) 100X (c). Tc metal (light spots) can be seen throughout the sample. The surface of the pellet is porous and deficient or free of Tc (arrow to side of (a)) and substantial porosity and fissures have formed, indicative of gas formation during sintering.

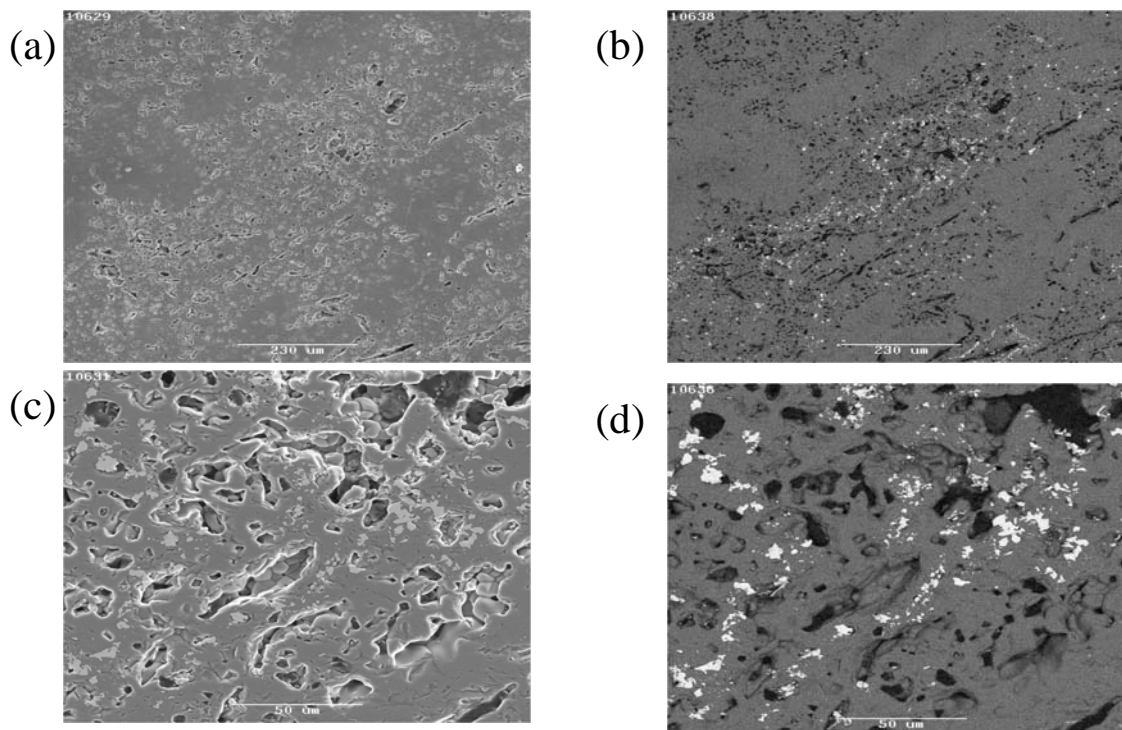


Fig. 4 SEM 100X (a) secondary electron (SEI) and (b) backscatter electron (BSE) micrographs and 500X (c) SEI and (d) BSE micrographs of the interior of the sample fired at 1350°C, Ar, 8 hours. The light phase in both pictures is Tc metal.

There are several key features of the samples:

- All of the samples have a surface layer on the pellets deficient in Tc. The thickness of the deficient layer increases from about 40-90  $\mu\text{m}$  at 1250°C to ~ 150-200  $\mu\text{m}$  at 1300°C and ~ 250-350 $\mu\text{m}$  at 1350°C.
- Tc metal forms somewhere between 1250 and 1300°C and becomes more extensive as the temperature increases. Associated with Tc metal is an increase in porosity in the interior of the sample culminating in large fissures in the samples sintered at 1350°C.
- The sample sintered at 1250°C contains regions that are Tc-rich, which have associated porosity and these are surrounded by regions that are deficient in Tc.

The evidence of volatilization from the surface of the pellets is not surprising given that Tc-O system diagrams published by Migge [20] indicate that the vapour pressure of  $\text{Tc}_2\text{O}_7$  that is produced via the equilibrium reaction  $4\text{TcO}_2 + 3\text{O}_2 = 2\text{Tc}_2\text{O}_7$  will be quite high under the atmosphere and temperatures used in this experiment, plus the fact that  $\text{TcO}_2$  is reported to be volatile above 900°C [8]. Given the low oxygen partial pressure of oxygen the argon gas ( $\sim 10^{-5}$  atm.) it is unlikely that significant losses are occurring purely from the oxidation of  $\text{TcO}_2$  to  $\text{Tc}_2\text{O}_7$  although this reaction may occur as oxygen is freed from the reduction of  $\text{Tc}^{4+}$  to metallic Tc. A significant quantity of the loss must be due to volatilization of  $\text{TcO}_2$ . The flowing Ar will compound the vapour loss. While the Tc-O phase diagram indicates that the  $\text{Tc}_2\text{O}_7$  vapour pressure should drop slightly with higher temperatures and lower  $P_{\text{O}_2}$ , the difference between 1250 and 1350°C is small. The increased time at temperature (due to the constant heating rates of 5 °C/min. employed), plus maybe some kinetic effects that increase the reactivity, would tend to increase the amount of surface volatilization as the temperature increases. The increase in the layer thickness with temperature indicates that the Tc can be removed from the rutile structure. From a production scale-up viewpoint the volatilization could be reduced by, e.g., using larger pellets to decrease the surface to volume ratios, optimising the firing schedule to decrease the time at temperature, e.g., fast-firing, improvements to the green microstructure of the pellet to improve reactivity, and the use of a static rather than a flowing atmosphere.

The formation of Tc-metal at  $\sim 1300^\circ\text{C}$  temperatures in Ar, where  $P_{\text{O}_2}$  is  $\sim 10^{-5}$  to  $10^{-6}$  atm. is consistent with Tc-O phase diagram data published by Migge [20], which indicates that the  $\text{TcO}_2$  – Tc boundary is close to this point. Large internal fissures in the pellet sintered at 1350°C/8h. indicate significant internal gas pressures forming during sintering at the higher temperatures. This is believed to be different from the surface loss discussed above, and associated with oxygen liberation from the reduction of Tc oxide to Tc metal. The result is different to that reported for perovskite [1,5], which retained  $\text{Tc}^{4+}$  after sintering for 1 hour at 1500°C and may indicate the absence of significant crystal chemical stabilisation in rutile but not in perovskite. Although the fissures are not present at 1250°C, this sample has regions in the microstructure rich in Tc, with associated porosity (Fig. 2b). This may be indicative of evaporation-condensation sintering mechanisms in the ceramic during the heating stage of the sintering cycle. This is thought to be possible given the high vapour pressure of  $\text{Tc}_2\text{O}_7$ , the phase field of which the sample passes during calcination and heating for sintering [20], or due to the volatilization of  $\text{TcO}_2$ . As mentioned above the median particle size of the Tiona AG raw material is  $\sim 2.5 \mu\text{m}$  and the distribution suggests that the particles are between 1 – 2  $\mu\text{m}$  with some agglomerates  $\sim 10 - 50 \mu\text{m}$  in size. The Tc-rich regions are  $\sim 50 - 100 \mu\text{m}$  across so clearly diffusion and

significant reaction has occurred, between the Tc and Ti raw materials. It is postulated that on drying the ammonium pertechnetate resides on the surface of the anatase powder, and forms Tc-oxide particles on calcination. However, it is not known at this stage when the Tc reacts with the  $\text{TiO}_2$  (anatase or rutile) to form a  $(\text{Tc,Ti})\text{O}_2$  solid solution. Hot pressing studies on the Tiona AG raw material [21] indicated that densification of the anatase starts at  $\sim 900$  - $1000^\circ\text{C}$  as the anatase to rutile transformation occurs, but that densification of the rutile is not completed until above  $1200^\circ\text{C}$ . Given that  $\text{TcO}_2$  is known to exhibit significant volatility above  $900^\circ\text{C}$  [8,20], it is desirable to incorporate the Tc into the  $\text{TiO}_2$  at lower temperatures and hence reduce its volatility. There are possible routes to achieve this end. For example, more intimate mixing of the Tc and Ti at the green stage, by improved milling, such that  $(\text{Tc,Ti})\text{O}_2$  solid solution reaction is completed faster and at a low temperature would be one such route. This would also reduce the sintering temperature required. Alternatively, processing routes utilising alkoxide/sol-gel chemistry would be capable of producing materials that will form the rutile and sinter at a lower temperature. It may also be possible to use sintering aids that reduce the sintering temperature of the  $\text{TiO}_2$ , via liquid phase sintering.

Further work needs to be carried out on controlling the redox conditions during sintering and optimising the sintering schedule. Buffers to control the redox would represent a start in this direction, but previous work with coarse NiO and Fe have not been entirely successful in that Tc-metal still formed.

## CONCLUSIONS

Preliminary studies attempting to form  $\text{Ti}_{0.9}\text{Tc}_{0.1}\text{O}_2$  via simple solid-state sintering routes in Ar have shown that Tc (presumed to be tetravalent) was readily incorporated into the rutile structure at  $1250$ ,  $1300$  and  $1350^\circ\text{C}$  to give regions close to the target composition, although at higher temperatures,  $1300$  and  $1350^\circ\text{C}$ , the oxygen partial pressure was sufficiently low that Tc metal also formed. The results are in agreement with published thermodynamic data for the Tc-O system indicating the absence of significant crystal chemical stabilisation of  $\text{Tc}^{4+}$  substitution in the  $\text{Ti}^{4+}$  site of rutile. The liberation of oxygen from the formation of the Tc metal creates large pores within the samples. However, even at  $1350^\circ\text{C}$  the core of the sample had regions with the target rutile composition. All the samples lost material from the surface of the pellet with the thickness of the layer becoming greater as the temperature increased. The data indicate that it is feasible to incorporate Tc in the tetravalent state in rutile or other titanate ceramics, but, the redox and temperature processing window may be small.

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## REFERENCES

- 1 K.P. Hart, E.R. Vance, R.A. Day, B.D. Begg and P.J. Angel, "Immobilization of Separated Tc and Cs/Sr in Synroc", *Matls. Res. Soc. Symp. Proc.*, **412**, 281-287, (1998).



- 2 R.D. Shannon, "Revised Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides", *Acta Cryst.*, " **A32**, 751 (1976).
- 3 E.R. Vance, K.P. Hart, M.L. Carter, M.J. Hambley, R.A. Day and B.D. Begg, "Further Studies of synroc immobilization of HLW Sludges and Tc for Hanford Tank Waste Remediation", *Matls. Res. Soc. Symp. Proc.*, **506**, 289, (1998).
- 4 E.R. Vance, K.P. Hart, R.A. Day M.L. Carter, M.J. Blackford and B.D. Begg, "Synroc Derivatives for the Hanford Waste Remediation Task", *Matls. Res. Soc. Symp. Proc.*, **465**, 341, (1997).
- 5 E.R. Vance, M.L. Carter, R.A. Day, B.D. Begg, K.P. Hart, and A. Jostsons, "Synroc and Synroc-Glass Composite Waste Forms for Hanford HLW Immobilization", pp. 2027-2039 in *Spectrum 96*, Aug. 18-23, Seattle, WA, USA 1996.
- 6 M. Yasser Khalil, *The Dissolution Kinetics of Technetium-Containing Glass and Spinel and of Fission Fragment-Damaged Actinide Host Phase*, Ph.D. thesis, Pennsylvania State University, Department of Nuclear Engineering, 1984.
- 7 M.Y. Khalil and W.B. White, "Dissolution of Technetium form Nuclear Waste Forms", pp. 655-662, in *Scientific Basis for Nuclear Waste Management VII*, Ed. G.L. McVay, Elsevier Science Publ. Co., New York, 1984.
- 8 O. Muller, W.B. White and R. Roy, "Crystal Chemistry of Some Technetium Containing Oxides", *J. Inorg. Nucl. Chem.*, **64**, 2075-2078, (1964).
- 9 C. Gaillard, N. Chevarier, N. Millard-Pinard, and P. Delichere, "Thermal Diffusion of Molybdenum in Apatite", *Nuclear Instruments and Methods in Physics Research, Section B, Beam Interactions with Materials and Atoms*, **161-163** [4] 646-650 (2000).
- 10 D.D. Keiser Jr., D.P. Abraham, J.W. Richardson Jr., "Influence of technetium on the microstructure of a stainless steel-zirconium alloy" *J. Nucl. Mater.*, **277**, [2-3], 333-338, (2000).
- 11 S.G. Johnson, D.D. Keiser, M. Noy, T. O'Holleran and S.M. Frank, "Microstructure and Leaching Characteristics of a Technetium Containing Metal Waste Form", *Matls. Res. Soc. Symp. Proc.*, **556**, 953-960, (1999).
- 12 T.M. Gilliam, R.D. Spence, B.S. Evans-Brown, I.L. Morgan, J.L. Shoemaker and W.D. Bostick, "Performance Testing of Blast Furnace Slag for Immobilization of Technetium in Grout," pp. 109-11, *Proc. SPECTRUM '88*, International Topical Meeting on Nuclear and Hazardous Waste Management, Pasco, WA, Sept.11-15, 1988, American Nuclear Society, Inc., La Grange Park, IL, 1988.

- 13 E.W. McDaniel, O.K. Tallent, T.L. Sams, W.D. Bostick and D.B. Delzer, "Basis for Selecting Cement-Based Waste Forms for Immobilizing Radioactive Waste," *Matls. Res. Soc. Symp. Proc.*, **127**, 421-430, (1989).
- 14 G.D. Del-Cul, I.L Morgan, W.D. Bostick, and P.E Osborne, *Grout-based waste forms for the solidification of anion-exchange resins. Final report.* Dec. 1991. 29 p. Oak Ridge Report No. K/TCD—1004, DOE Contract AC05-84OT21400, Oak Ridge K-25 Site, TN, USA, 1991.
- 15 P.G. Allen, J.J. Bucher, N.M. Edelstien and D.K. Shuh, "X-ray Absorption Fine Structure Studies of <sup>99</sup>Tc Speciation in Cements", pp. 63-74 in *Proceedings of workshop on Long-Lived Radionuclide Chemistry in Nuclear Waste Treatment*, Villeneuve-les-Avignon, France, 18-20 June 1997, NEA/OECD, Paris, 1998.
- 16 D. Singh, V.R. Mandalika, A.S. Wagh and M. Tlustochowicz, *Immobilization of <sup>99</sup>Tc in Low-temperature Phosphate Ceramic Waste Form*, US report ANL/ET/CP--92582; CONF-970568—11, Argonne National Laboratory, May 1997.
- 17 E. Freude, W. Lutze, C. Russel and H.A. Schaeffer, "Investigation of The Redox Behaviour of Technetium in Borosilicate Glass Melts by Voltammetry", *Matls. Res. Soc. Symp. Proc.*, **127**, 199-204, (1989).
- 18 A. Jouan, J.P. Moncouyoux and S. Halaszovich, "Reduction of Ru and Tc Volatility During Vitrification by Denitration", pp. 153-161 in *Denitration of Radioactive Liquid Waste*, Ed. L. Cecille and S. Halaszovich, Graham And Trotman, London, 1986.
- 19 N.E Bibler, T.L. Fellingner, S.L. Marra, R.J. O'Driscoll, J.W. Ray and W.T. Boyce. *Tc-99 and Cs-137 volatility from the DWPF production melter during vitrification of the first macrobatch at the Savannah River Site*, US report, WSRC-MS-99-00860, Westinghouse Savannah River Company, April 14, 2000.
- 20 H. Migge, "Thermodynamic Comparison of the Systems Re-O and Tc-O", *Matls. Res. Soc. Symp. Proc.*, **127**, 205-213, (1989).
- 21 M.W.A. Stewart, D.S. Perera and C.C. Sorrell, "Constant Heating Rate Hot-Pressing of Titanate Ceramics", *Proceedings PacRim 2, The Second International Meeting of Pacific Rim Ceramic Societies*, 15-17 July 1996, Cairns Australia, Ed. P. Walls, C. Sorrell and A. Ruys, International ceramic Monographs, Volume 2, CD-ROM, The Australasian Ceramic Society, Sydney, 1998.