

Short Communication

A Study of a Surrogate Nuclear Thermal Propulsion Fuel Element

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received March 8, 2023; received in revised form May 11, 2023; accepted May 23, 2023

Abstract

A surrogate fuel, zirconium carbide/titanium nitride, has been prepared using a simple method to obtain a more uniform distribution of titanium nitride in the zirconium carbide matrix. Powders were sintered using spark plasma sintering at 2 023 K and 2 123 K using a modified sintering profile. This resulted in a fairly uniform distribution of titanium nitride in the zirconium carbide matrix with a density of 95 % of theoretical at 2 123 K. Scanning electron microscopy, indentation hardness and X-ray diffraction results are given.

Keywords: Carbide, nitride, spark plasma sintering, X-ray diffraction, propulsion fuel element

I. Introduction

Long-duration spaceflight can expose astronauts to two major problems. These are extended periods of weightlessness and radiation exposure¹. Therefore, it is necessary to develop alternate means of propulsion to that of chemical propulsion. One option being studied is Nuclear Thermal Propulsion (NTP). NTP offers benefits over chemical propulsion, such as a higher specific impulse ($I_{sp} \sim 900$ s), which is twice that of chemical propulsion, a higher thrust-to-mass ratio, better tolerance to payload mass growth and architecture, and lower initial mass in low Earth orbit². As an example, when Mars has its closest approach to Earth, chemical propulsion would see a transit of 150 to 300 days, while NTP would be half of that.

At present, there are several fuel element systems under consideration including CERMETS, tricarbitides and TRISO fuels. Advanced solid solution, tricarbitides fuels such as (U, Zr,Nb)C have been proposed for NTP due to their expected long life, and higher operating temperature³. In one study, these mixed carbides of varying compositions were cold-pressed and sintered using a graphite susceptor³. They achieved liquid phase sintering above 2 800 K and densities greater than 95 % of theoretical. W/UN₂ and UN/Mo systems have also been studied^{4,5}. The W/UN₂ system shows promise, however, tungsten has a high neutron absorption, which can limit the fuel efficiency. TRISO-derived fuel compacts have also been considered for use as an NTP fuel due to their low parasitic neutron absorption⁶. Another system receiving considerable attention is uranium nitride (UN) particles distributed in a zirconium carbide (ZrC) matrix. ZrC has good neutron absorption properties compared to metals used in CERMETS and UN has a high uranium loading factor.

These properties give it an advantage over other possible fuel choices. To determine if a previously used binder method can be used on this system, we tested it on the zirconium carbide/titanium nitride (ZrC/TiN) surrogate system^{7,8}. In this system, the ZrC is the matrix material. Use of a binder was shown to prevent segregation of particles of disparate size and density.

Spark Plasma Sintering (SPS), a subset of electrical-field-assisted sintering, has been demonstrated to be a viable alternative to traditional sintering methods^{9–11}. SPS can produce high densities at lower temperatures and processing times with minimized grain growth as compared to traditional sintering methods such as furnace sintering and hot isostatic pressing^{9–11}. It has been demonstrated using traditional sintering methods that pores located on grain faces have greater mobility than those at grain corners and ultimately end up within the grains^{12,13}. The advantages of SPS over traditional sintering methods are lower sintering temperatures, short dwell times (minutes versus hours) and rapid heating rates, all of which result in smaller more uniform grain sizes as well as energy savings.

In SPS, the powder is heated by Joule heating resulting from passing a current through a graphite die and the powder during sintering¹⁴.

The present study looks at the SPS-densification of ZrC/TiN, which is a surrogate for ZrC/UN.

II. Experimental

ZrC powder was obtained from Alfa Aesar. The powder has a particle size ranging from 1–5 microns. TiN powder was purchased from American Elements and has an average particle size of 75 microns. The particle size and size range for both powders were as stated by the manufacturers. The TiN particles are angular in shape. TiN was chosen as a surrogate for UN due to the same crystal structure and similar melting points. A powder

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processing method developed for W/VO₂ was applied to the present materials^{7,8}. In this method, low-molecular-weight polyethylene powder (Honeywell) was milled to approximately 1 micron. Next, a 50-gram mixture of 50 vol% ZrC and 50 vol% TiN and 0.5 wt% low-density polyethylene powder were thoroughly mixed for 1 hour in a Turbula (W.A. Bachhofen). The mixing in the Turbula is multi-axis, which allows for more thorough mixing of the powders. The mixed powder was then placed in a 400-ml Pyrex beaker and then stirred on a hot plate for 10 minutes above the drop point of the polyethylene (374 K), before being cooled to room temperature. All processing was performed in an argon-filled glovebox.

Approximately 5 grams of this mixture was then placed in a 12-mm-diameter graphite die in an argon-filled glovebox. The dies were wrapped in parafilm sealing tape (paraffin wax/polyethylene) before being transferred to the SPS. The parafilm was removed just before the dies were loaded into the SPS chamber. Samples were sintered at 2 023 K and 2 123 K in a Dr. Sinter SPS. The furnace profile used during densification was as follows: Samples were heated at a rate of 100 K/min to 100 K below the final sintering temperature, then heated at a rate of 50 K/min to the final sintering temperature to prevent the temperature from overshooting. The pressure was increased at a rate of 10 MPa/min to the final pressure of 50 MPa. The sample was held at the sintering temperature for 20 minutes and then allowed to cool to room temperature.

Density was obtained using the Archimedes method, which has an accuracy of ± 0.1 g/cm³. Three samples from each sintering temperature were measured. The densities were averaged for each sintering temperature. Scanning electron microscopy and energy-dispersive X-ray (FEI Quanta FEG 650, with AMATEK PV7000/10) was performed on each sample. X-ray diffraction was performed (Bruker D8 Advance, or Rigaku SmartLab using a Cu_{K α 1} radiation source: $\lambda = 1.54056$ Angstroms) to determine the crystal phases in the sintered samples. Hardness was determined using a Vickers microhardness tester (Leco LM Series 310) using a force of 9.81 Newtons.

The samples densified at 2 023 K were 92 % of theoretical while the samples densified at 2 123 K had a density of 95 % of theoretical.

III. Results

Fig. 1 shows the TiN particles coated with the ZrC powder. The angular nature of the TiN particles can be seen, which plays a role in how well the distribution of TiN is in the ZrC matrix after densification. Although the TiN particles have a mean size of 75 microns, the image shows particles larger than 75 microns. These larger features are

due to clumping of the TiN and ZrC particles caused by the polymer binder.

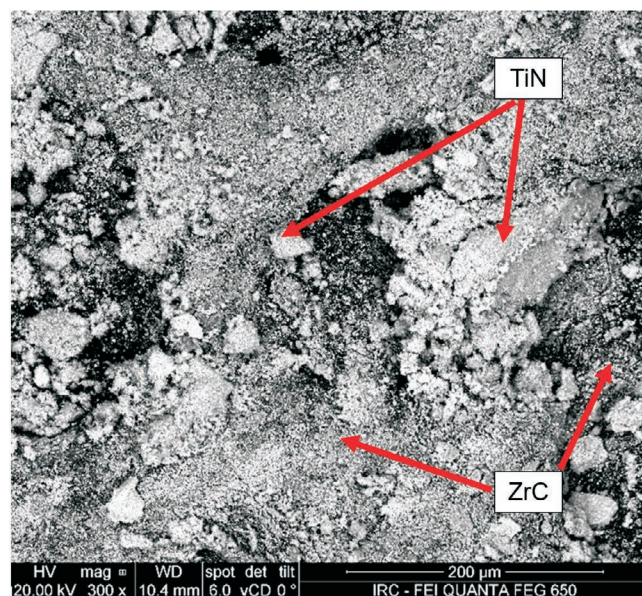


Fig. 1: Scanning electron image (secondary electrons) of the TiN particles coated with ZrC powder.

Fig. 2a is an SEM image (secondary electron) of the ZrC/TiN material after sintering at 2 123 K, and the associated EDS map (Fig. 2b). The distribution of TiN in the ZrC matrix is not totally uniform in this image, the reddish orange is Ti, and blue green is Zr. The associated pie chart gives the distribution of elements and their weight percentages. As can be seen from the pie chart, there is oxygen present. There is segregation of some of the TiN particles. Ideally, one would like to see none of the TiN particles in contact with each other, but separated by the ZrC matrix. Individual element maps can be found in supporting information. It is noted that oxygen is primarily associated with the Zr phase, which is also noted in the XRD in Fig. 3.

Fig. 3 shows the XRD of a sample sintered at 2 023 K. The inset table outlines the Crystallography Open Database reference spectra used (COD REV212673 2018.12.20).

It can be seen that along with titanium carbide (TiC) and zirconium nitride (ZrN), zirconium oxide (ZrO₂) is present in two phases. Control scans of the precursor TiN and ZrC powders were performed. As can be seen from these scans, there is no oxygen present in the starting powders.

The XRD patterns of the ZrC/TiN sample sintered at 2 123 K are shown in Fig. 4.

The hardness of the sample sintered at 2 023 K was 18.33 ± 0.01 GPa, while the hardness of the sample sintered at 2 123 K was 19.60 ± 0.01 GPa.

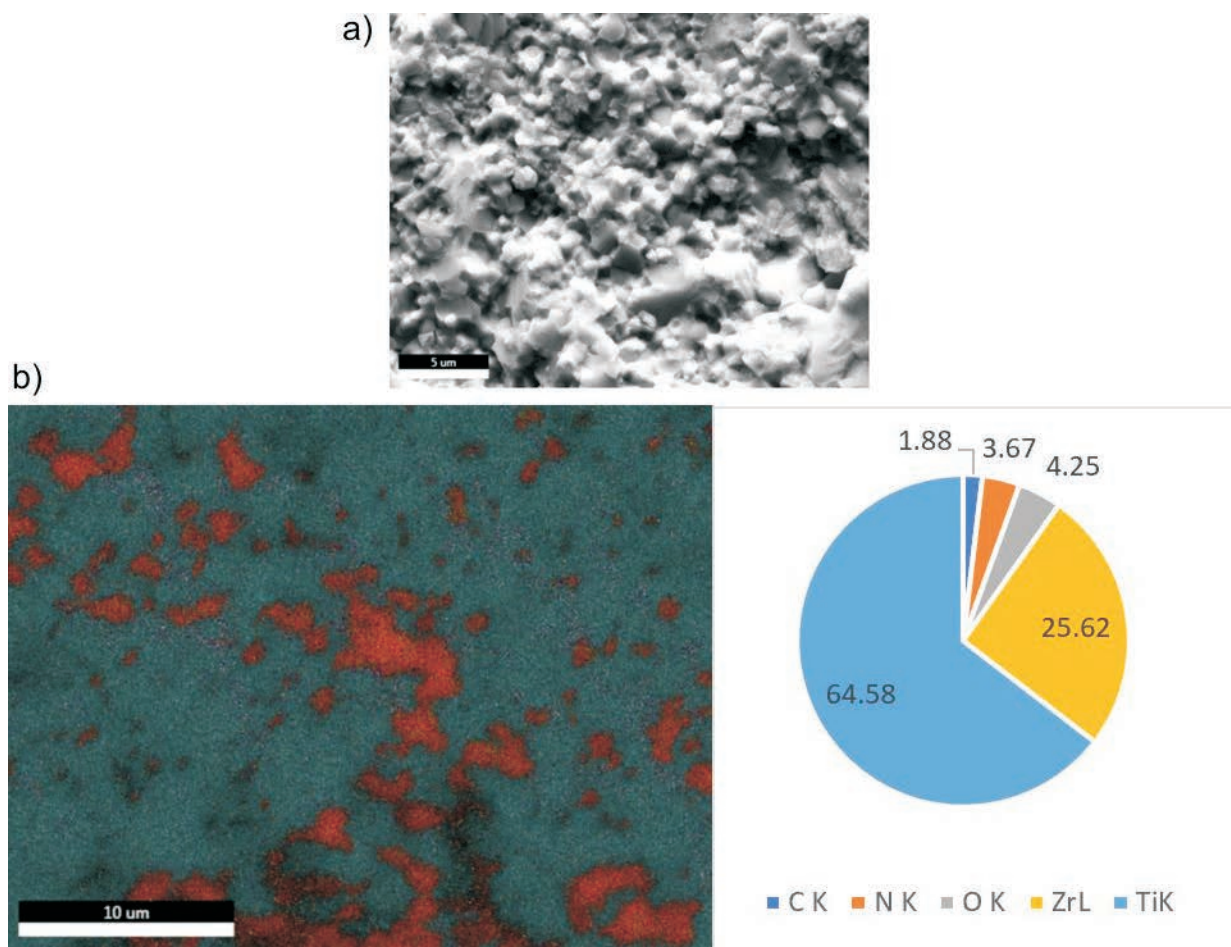


Fig. 2: Secondary electron image of ZrC/TiN sintered at 2 123 K on left, EDS map on right. Red is Ti, blue is Zr, green is oxygen.

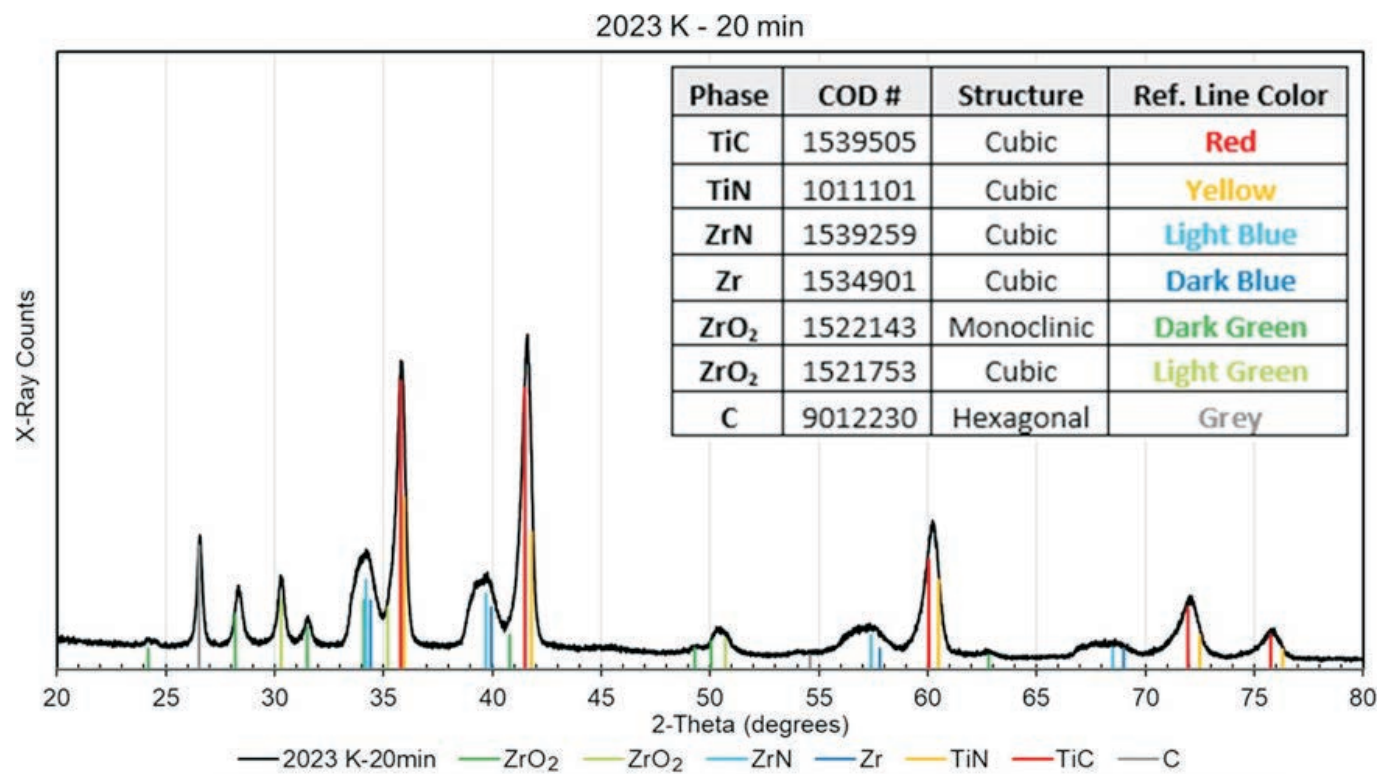


Fig. 3: XRD spectra of ZrC/TiN sample sintered at 2 023 K for 20 minutes.

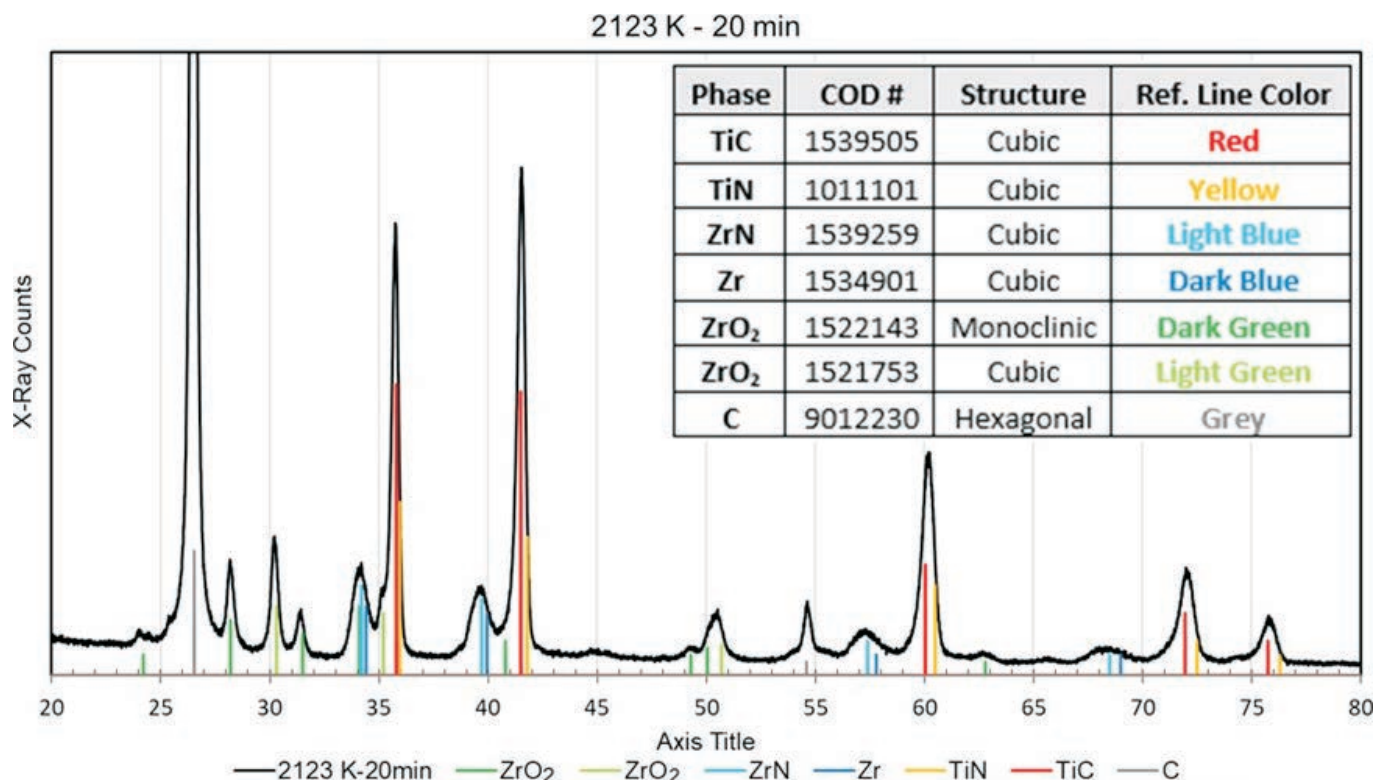


Fig. 4: XRD spectra of ZrC/TiN sintered at 2123 K for 20 minutes.

IV. Discussion

As can be seen from Fig. 1, it appears that the ZrC powder is coating the larger TiN particles. However, once sintered there is some segregation of ZrC and TiN as seen in Fig. 2. It is thought that this is due to the non-spherical shapes of the TiN particles. In a previous study, using tungsten particles of 5–15 micrometers in diameter and nearly spherical hafnium oxide particles of ~150 micrometers in diameter, it was found that the tungsten completely coated the much larger hafnium oxide particles resulting in a uniform distribution of hafnium oxide in a tungsten matrix when sintered⁷. Also, in a follow-up study which replaced the hafnium oxide particles with depleted uranium dioxide (nearly spherical) particles, a uniform distribution of the uranium dioxide in the tungsten matrix was also observed⁸. The difference in the particle distribution from these previous studies and the present study is most likely due to the angular shape of the TiN particles. It can be envisioned that, when the powders and the polyethylene binder are being stirred and heated above the polymer drop point, having the larger particles being nearly spherical rather than angular will result in a more uniform coating of the smaller matrix material. Unfortunately, only angular TiN could be purchased in the larger particle size. The large particle size of TiN was used to simulate the large UN particles which are under study at the present.

The densities for the two sintered samples are less than theoretical. The sample sintered at 2123 K is 95 % of theoretical. In fuels such as UN/ZrC, it is better to have densities below theoretical to allow for swelling due to fission gas.

The X-ray diffraction studies of the sintered ZrC/TiN composite led to unexpected results. As can be seen from Figs. 3 and 4, there is no evidence of substantial ZrC in the sintered materials. Rather, peaks for ZrO₂, ZrN, Zr, TiN, TiC and carbon were in evidence. Given the similarity between the TiC and TiN peaks, presence of a TiCN phase may also be possible. Oxygen contamination can readily explain the presence of the ZrO₂ peaks. This oxygen contamination could have occurred during the transfer of the die to the SPS chamber when the parafilm was removed from the die, or possibly from oxidation of one or more of the precursor powders. The titanium appears to have bonded readily with the carbon, leaving pure zirconium and titanium carbide. Due to this unexpected result, it was decided to sinter a sample of ZrC and pure titanium metal (Alfa Aesar, 40 micron) at 2123 K for 20 minutes under 50 MPa pressure and perform X-ray diffraction, shown in Fig. 5. Here, it is noted that the Ti metal does bond carbon, to become TiC, and ZrC is noted only in trace amounts, while Zr metal is left behind in significant quantity. It is noteworthy that no ZrO₂ peaks are found in this pattern. An associated secondary electron image and EDS map is shown in Fig. 6. These results differ from other studies. For example, in reference 15, ZrN, carbon black and TiC powders were sintered via SPS at 2173 K for 10 minutes at 40 Mpa. They found distinct peaks of TiC, ZrC and carbon using XRD. Ryu *et al.* doped ZrC, TiC and ZrN with 20 wt% Dy₂O₃ and sintered it by means of SPS¹⁶. XRD showed distinct peaks, indicating Dy₂O₃ and each matrix phase maintained their original nature after sintering.

It can be seen from Fig. 5 that there are TiC peaks in two phases, large Zr peaks and very small ZrC peaks are present. This confirms the idea that carbon seeks the Ti

during sintering and suggests that in Fig. 4, ZrC is either not present, or in such a small amount that any peaks are too small to note when compared to the more dominant TiC, Zr, ZrN and carbon peaks. This has implications for sintering ZrC/UN, which could affect the efficiency of the proposed composite fuel. One could end up with a sub-stoichiometric UN leading to excess uranium in the fuel, which would lead to diffusion of the uranium into grain boundaries. This in turn would lead to mechanical stresses in the fuel and possible fuel failure. Also, UC could be formed with this excess uranium. This redistribution of elements after sintering could also help explain why some segregation shows up in the sintered samples.

Fig. 6 shows a secondary electron image of a ZrC/Ti sample fracture surface on the left. On the right is the

associated EDS map showing a uniform distribution of the elements in the secondary electron image.

The hardness values of the two samples were compared to literature values for TiC, TiN, ZrO₂ and carbon. Reference 17 reported a hardness value of 25.2 GPa for TiC, while reference 18 reported a value of 31.38 GPa. A TiC/TiN composite had a value of 16 GPa¹³. A value of 19.61 GPa was reported for bulk-sintered TiN¹⁹. The Vickers hardness for pure ZrO₂ was reported to be 11.77 GPa²⁰. Carbon has a Mohs hardness of 5, which can be estimated to approximately 3.8 GPa²¹. Pure zirconium has a Vickers hardness of 900 MPa²². The Vickers hardness for ZrN was reported as 15 GPa²³. Considering, these compounds and elements are present in the sintered samples and that TiC appears to be the dominant phase, then our hardness values are accurate for our samples.

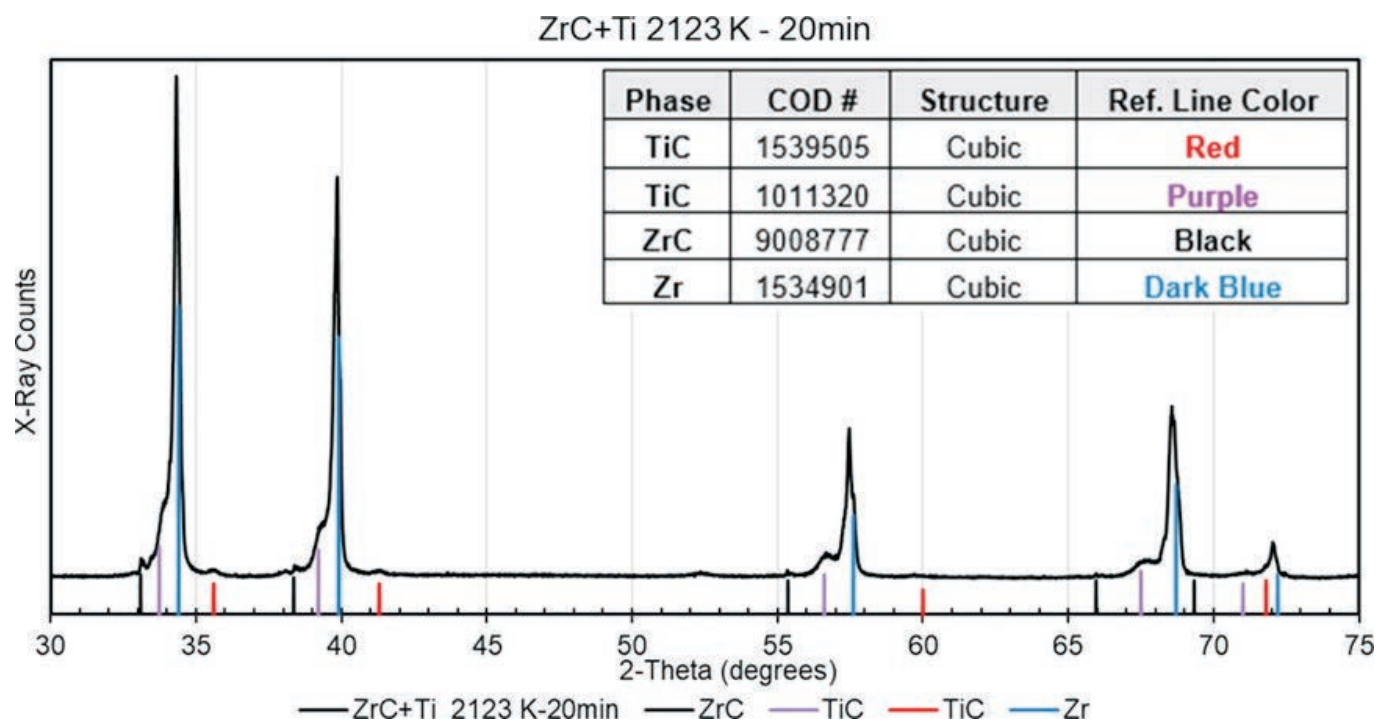


Fig. 5: ZrC/Ti sintered at 2 123 K for 20 minutes.

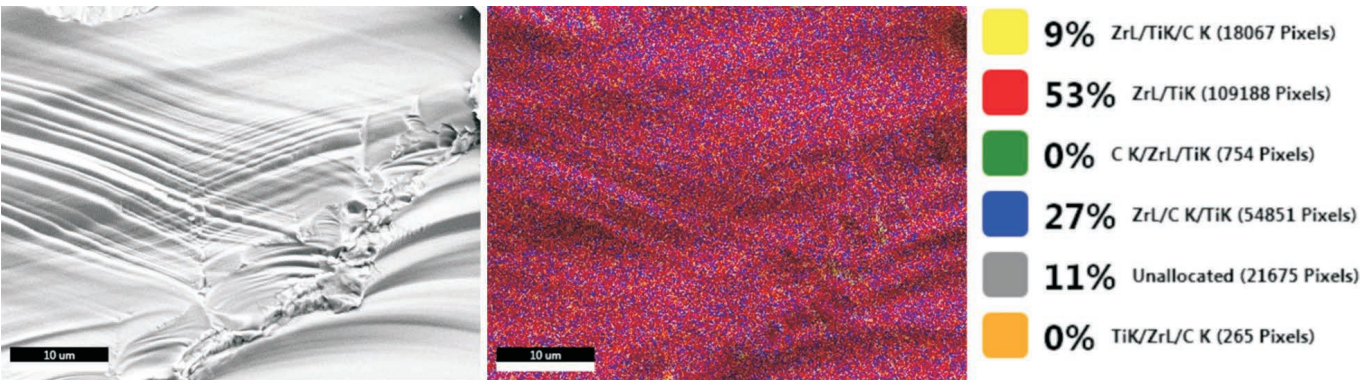


Fig. 6: Secondary electron image of ZrC/Ti and associated EDS data.

V. Conclusions

To summarize, we have found an unexpected mixture of compounds and elements in our sintered samples, which may have implications for sintered ZrC/UN. Thermodynamically, TiN and UN have similar values of specific heat and enthalpy^{24,25}. Both are also cubic crystal structure and have similar melting points and sintering temperatures. These similarities lead us to conclude that sintering of ZrC/UN will also result in a mixture of compounds as seen in this study. However, a sintering study of ZrC/UN should be performed with appropriate analysis to confirm this conclusion.

ZrC/TiN was sintered using SPS at 2 023 K and 2 123 K. The density increased from 92 % to 95 % of theoretical with the increase in temperature. Hardness values also increased. X-ray diffraction results were surprising, showing no sign of ZrC in the sintered samples. SEM images showed some segregation of the TiN particles within the matrix which was explained by the non-spherical nature of the TiN particles.

Acknowledgements

The authors would like to acknowledge the NASA Space Nuclear Project for funding this study.

References

- Tucker, D.S.: Using Spark Plasma Sintering to Produce Nuclear Propulsion Fuel Elements, *Advances in Composite Materials Development*, 978–1-78984–130–5, 2019
- Tucker, W.C., Chowdhury, P., Abbott, L.J., Haskins, J.B.: Toward an In-Depth Material Model for CERMET Nuclear Thermal Rocket Fuel Elements, *Nucl. Tech.*, **207**, 825–835, (2021).
- Knight, T.W., Anghaie, S.J.: Processing and Fabrication of Mixed Uranium/Refractory Metal Carbide Fuels with Liquid Phase Sintering, *J. Nucl. Mater.*, **306**, 54–60, (2002).
- Gates, J.T., Denig, A., Ahmed, R., Mehta, V.K., Kotlyar, D.: Low-Enriched CERMET-Based Fuel Options for Nuclear Thermal Propulsion Engine, *Nucl. Eng. Design.*, **331**, 313–330, (2018).
- Ratfery, A.M., Seibert, R., Brown, D., Trammell, M., Nelson, A., Terrani, K.: Fabrication of UN-Mo CERMET using Advanced Manufacturing Techniques, NETS, April 6–9, 2020.
- Houts, M.G., Joyner, C.R., Abrams, J., Witter, J., Venneri, P.: Versatile Nuclear Thermal Propulsion (NTP), 70th Intern. Astronautical Congress, Oct. 21–25, 2019.
- Tucker, D.S., Barnes, M.W., Hone, L., Cook, S.: High Density Uniformly Distributed W/VO₂ for use in Nuclear Thermal Propulsion, *J. Nucl. Mater.*, **486** 246–249 (2017).
- Tucker, D.S., Wu, Y., Burns, J.: Uranium Migration in Spark Plasma Sintered W/VO₂ CERMETS, *J. Nucl. Mater.*, **500**, 141–144, (2018).
- O'Brien, R.C., Ambrosi, R.M., Bannister, N.P., Howe, S.D., Atkinson, H.V.: Safe Radioisotope Thermoelectric Generators and Heat Sources for Space Applications, *J. Nucl. Mater.*, **377**, 506–521, (2008).
- Wang, X., Xie, Y., Guo, H., Blest, O., Van der, Vleugels, J.: Sintering of WC-Co Powder with Nanocrystalline WC by Spark Plasma Sintering, *Rare Met.*, **25**, 246–250, (2006).
- Nguyen, V-H., Delbari, S.A., Asl, M.S., Le, Q.V., Jang, H.W., Shokouhimehr, M., Mohammadi, M.: A Novel Spark Plasma Sintered TiC-ZrN-C Composite with Enhanced Flexural Strength, *Ceram. Int.*, **46**, 29022–29032, (2020).
- Ryu, H.J., Lee, Y.W., Cha, S.I., Hong, S.H.: Sintering Behavior and Microstructures of Carbides and Nitrides for Inert Matrix Fuel by Spark Plasma Sintering, *J. Nucl. Mater.*, **352**, 341–348, (2006).
- Atkinson, H.V., Davies, S.: Fundamental Aspects of Hot Iso-static Pressing: An Overview, *Metall. Mater. Trans. A*, **31**, 2981, (2000).
- Carpay, F.M.A.: The effect of pore drag on ceramic microstructures, in: *Proceedings of Ceramic Microstructures '76*, Westview, Boulder CO, 1977, p. 171, ISBN: 0306426811.
- German, R.M.: *Sintering Theory and Practice*, John Wiley, New York, 1996, ISBN 0–471–05786-X.
- O'Brien, R.C., Ambrosi, R.M., Bannister, N.P., Howe, S.D., Atkinson, H.V.: Spark Plasma Sintering of Simulated Radioisotope Materials with Tungsten CERMETS, *J. Nucl. Mater.*, **393**, 108, (2009).
- Teber, A., Schoenstein, F., Tetard, F., Abdellaoui, M., Jouini, N.: Effect of SPS Process Sintering on Microstructure and Mechanical Properties of Nanocrystalline TiC for Tools Application, *Intern. J. Refract. Met. H.*, **30**, 64, (2012).
- Shackelford, J.F., Alexander, W.: *CRC materials and science engineering handbook*: CRC press, 2010.
- Liu, N., Xu, Y.D., Li, H., Li, G.H., Zhang, L.D.: Effect of Nano-Micro TiN Additions on the Microstructure and Mechanical Properties of TiC Based CERMETS, *J. Eur. Ceram Soc.*, **22**, 2409, (2002).
- Moshtaghioun, B.M., Gomez-Garcia, D., Dominguez-Rodriguez, A.: Exotic Grain Growth Law in Twinned Boron Carbide under Electric Fields, *J. Eur. Ceram Soc.*, **38**, 1190, (2018).
- Kuwahara, H., Mazaki, N., Takahashi, M., Watanabe, T., Yang, X., Aizawa, T.: Mechanical Properties of Bulk Sintered Titanium Nitride Ceramics, *Mater. Sci. Eng. A*, **319–321**, 687, (2001).
- Kawai, N., Lin, J., Youmaru, H., Shinya, A.: Effect of Three Luting Agents and Cyclic Impact Loading on Shear Bond Strengths to ZrO₂ with Tribochemical Treatment, *J. Dent. Sci.*, **7**, 118, (2012).
- Kinney, G.F.: *Engineering Properties and Applications of Plastics*, John Wiley and Sons, New York, 1957.
- Oetting, F.L., Leitnaker, J.M.: The Chemical Thermodynamic Properties of Nuclear Materials I: Uranium Mononitride, *J. Chem. Thermodyn.*, **4**, 199, (1972).
- NIST Chemistry Webbook, SRD 69, Titanium Nitride.