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Title

Microstructural Characterization of a Thin Film ZrN Diffusion Barrier in an As-Fabricated U–7Mo/Al Matrix Dispersion Fuel Plate

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Abstract

The United States High Performance Research Reactor Fuel Development program is developing low enriched uranium fuels for application in research and test reactors. One concept utilizes U-7 wt.% Mo (U-7Mo) fuel particles dispersed in Al matrix, where the fuel particles are coated with a 1 μm -thick ZrN coating. The ZrN serves as a diffusion barrier to eliminate a deleterious reaction that can occur between U-7Mo and Al when a dispersion fuel is irradiated under aggressive reactor conditions. To investigate the final microstructure of a physically-vapor-deposited ZrN coating in a dispersion fuel plate after it was fabricated using a rolling process, characterization samples were taken from a fuel plate that was fabricated at 500°C using ZrN-coated U-7Mo particles, Al matrix and AA6061 cladding. Scanning electron and transmission electron microscopy analysis were performed. Data from these analyses will be used to support future microstructural examinations of irradiated fuel plates, in terms of understanding the effects of irradiation on the ZrN microstructure, and to determine the role of diffusion barrier microstructure in eliminating fuel/matrix interactions during irradiation. The as-fabricated coating was determined to be cubic-ZrN (cF8) phase. It exhibited a columnar microstructure comprised of nanometer-sized grains and a region of relatively high porosity, mainly near the Al matrix. Small impurity-containing phases were observed at the U-7Mo/ZrN interface, and no interaction zone was observed at the ZrN/Al interface. The bonding between the U-7Mo and ZrN appeared to be mechanical in nature. A relatively high level of oxygen was observed in the ZrN coating, extending from the Al matrix in the ZrN coating in decreasing concentration. The above microstructural characteristics are discussed in terms of what may be most optimal for a diffusion barrier in a dispersion fuel plate application.

Keywords

irradiation testing; nuclear fuel; research reactor; uranium molybdenum alloy

Classification Codes

4: Fission reactor cladding and structural materials

4.1: Zirconium and zirconium alloys

1 Introduction

The High Performance Research Reactor Fuel Development (HPRRFD) program, sometimes called the Reduced Enrichment for Research and Test Reactor (RERTR) program, is developing low-enriched uranium (LEU) fuels for application in research reactors.[1] U-7 wt.% Mo (U-7Mo) alloy dispersion fuel, with approximately 55 volume percent U-7Mo fuel phase, is one type being developed.[2] It has been observed that during irradiation at aggressive reactor conditions, interaction can occur between the fuel and matrix that results in development of an interaction layer that is unstable under irradiation, which can contribute to fuel plate failure [3]. In order to eliminate this deleterious fuel/matrix interaction, a diffusion barrier is being evaluated for deposition on the U-7Mo fuel particles before the coated fuel particles are used for fuel plate fabrication[3]. Zirconium mononitride (ZrN) is a possible candidate diffusion barrier material. ZrN is a IV-B transition metal nitride with a face-centered cubic (FCC) crystal structure (NaCl structure), a lattice parameter of 4.57 Å, a hardness as high as 25 GPa, and a Young's modulus that can be as high as 400 GPa [G. W. Egeland, J. A. Valdez, S. A. Maloy, K. J. McCellan, K. E. Sickafus, and G. M. Bond, "Heavy-ion irradiation defect accumulation in ZrN characterized by TEM, GIXRD, nanoindentation, and helium desorption," J. Nucl. Mater. 435 (2013) 77-87.] It has a high melting temperature (2952°C) a density of 7.09 g/cc [Lide, David R., ed. (2009). *CRC Handbook of Chemistry and Physics* (90th ed.). Boca Raton, Florida: CRC Press. ISBN 978-1-4200-9084-0], and a thermal expansion coefficient of $7.24 \times 10^{-6} \text{ K}^{-1}$ [Cheng-Shi Chen, Chuan-Pu Liu, C.-Y.A. Tsao, Heng-Chieh Yang, "Study of mechanical properties of PVD ZrN films, deposited under positive and negative substrate bias conditions," Scripta Mat. 51 (2004) 715-719.]. As a IV-B transition-metal nitride, ZrN can be produced as a thin film that, besides having a high hardness and melting point, also exhibits chemical stability, corrosion resistance, low resistivity and low coefficient of friction. Overall, the transition-metal nitrides are very attractive compounds because of their excellent mechanical, thermal, electrical, and catalytic properties.[4] The IV-B transition-metal nitrides have been investigated as diffusion barriers in metallization schemes, superlattice constituents, field emitters, electrical contacts to III-V semiconductors, Josephson junctions, and cryogenic thermometers.[5] ZrN, specifically, has been used for many industrial applications, including hard coatings, diffusion barriers in semiconductor technologies, optical applications for heat mirrors, and decorative coatings.[4]

During the deposition of a ZrN coating on U-7Mo powders using low temperature physical vapor deposition (PVD), individual atoms are being deposited such that a low dimensional material is being created by condensing, one by one, atomic/molecular/ionic species of matter. Since the final thickness is less than a few microns, it can be considered to be a thin film. In general, a thin film is defined as different from a thick film, which is thought of as a low-dimensional material created by thinning a three dimensional material or assembling large clusters, aggregates, or grains of atomic, molecular, or ionic species.[6] Thin films are generally considered as coatings that are used to modify and increase the functionality of a bulk surface or substrate. They are used to protect surfaces from wear, to improve lubricity, to improve corrosion and chemical resistance, and to provide a barrier to gas penetration. In many cases, thin films do not affect the bulk properties of the material.[7]

Thin films have distinct advantages over bulk materials. Because most processes used to deposit thin films are non-equilibrium in nature, the composition of thin films is not constrained by metallurgical phase diagrams. Crystalline phase composition can also be varied to a certain extent by deposition conditions and plasma enhancement. Virtually

every property of the thin film depends on and can be modified by the deposition process, and not all processes produce materials with the same properties. The basic properties of film, such as film composition, crystal phase and orientation, film thickness, and microstructure are controlled by the deposition conditions. As a result, thin films exhibit unique properties that cannot be observed in bulk materials.[6] Thin films exhibit a wide variety of microstructures, characterized in terms of grain size and crystallographic orientation, lattice defects, phase composition, and surface morphology.[8] A single material can be used in several different applications and technologies, and the optimum properties for each application may depend on the deposition process used. Since not all deposition technologies yield the same properties or microstructures, the deposition process must be chosen to fit the required properties and application. The choice of deposition technique is determined by the application for the coating, the desired coating properties, cost or production rate available from the process, temperature limitation of the substrate, uniformity or consistency of the process, and its compatibility with subsequent processing steps. The chemical and physical conditions during the deposition reaction can strongly affect the resultant microstructure of the coating.[9] The correct material for application as a thin film barrier must be found empirically.[10] One reason is that the values of the parameters derived from measurements on bulk materials generally do not apply to thin films, where the conditions of stress and structure differ from those of bulk material. Also, the possibility exists that undetected chemical impurities will alter the film properties. It should be recognized that no material will act as a barrier indefinitely, so the service conditions where breakdown occurs needs to be identified.

Traditionally, vacuum processes that produce polycrystalline films have been used for the deposition of transition-metal nitrides. Magnetron sputtering is a useful method for the deposition of these materials due to a high rate of deposition, reduced operating pressures and increased energetic bombardment of the substrate. The deposition techniques most commonly used include ion-assisted deposition, reactive magnetron sputtering, dual-ion beam sputtering, ion plating, and plasma-enhanced chemical vapor deposition.[5] For cases when coatings are to be applied to powders, a barrel sputtering system can be employed.[11] A barrel sputtering system, called Sputtering Tool for Engineering Powder Surfaces & Deposition Reactor for Uranium based Model System (STEPS&DRUMS), has been developed to deposit ZrN on U-7Mo particles.[12,13] This system utilizes reactive magnetron sputtering, which is a PVD process whereby atoms are ejected from a target (at near room temperature) through the impact of ions. Reactive sputtering is an advantageous method for formation of complex products from the reaction of elemental metal targets and reactive gases. This eliminates the need for construction of expensive compound targets or the use of highly volatile gases. This technique has been used to generate a host of other high quality nitrides (e.g., NbN, TiN, AlN).[5] The STEPS&DRUMS system has as a major component, a drum that is mounted inside a vacuum chamber on two rotational support axes, one of which is powered by a motor outside of the vacuum. This allows rotation of the drum with speeds up to four rotations per minute. Powder is placed inside the drum, which is continuously agitated by the rotational action. On the large flange of the vacuum vessel, up to three water-cooled magnetron sputter heads are mounted inside the rotational drum. The targets are 3 inches in diameter and can be any type of metallic material. This allows simultaneous use of

several sputter guns with the same target material for increased deposition speed and/or the use of different targets for co-deposition or multi-layer deposition without breaking the vacuum. As atoms pass through the vacuum during the process and deposit on the surface of the U-7Mo particles while they rotate in the turning drum, a film is formed, and the heating of the particles is avoided.[12]

Microstructural characterization has been performed on ZrN coating that has been deposited using STEPS&DRUMS, including the use of synchrotron radiation.[14]. The samples that were characterized were cylindrical compacts that were fabricated using U-7Mo fuel particles coated with ZrN (using the STEPS&DRUMS process) and Al powder. These samples were characterized after they had been annealed at 340°C for 130 days, 450°C for 4 hours, or 550°C for 2 and 4 hours. ZrN was detected in the samples (about 1.2 wt.%). Overall, the ZrN was observed to be heavily textured, and the authors of the paper hypothesized a strong relation to the U-Mo grains on which the ZrN was deposited. The development of some U-Mo particle oxidation was observed. Almost no U-Mo/Al matrix interaction was observed overall. Electron probe micro-analysis (EPMA) and scanning electron microscopy (SEM) have also been employed to characterize annealed compact samples that contained ZrN-coated U-7Mo and Al powder, along with samples from actual as-fabricated fuel plates.[13] The results of this work showed that no U-7Mo/Al interaction occurred during sample testing, except for the as-fabricated samples that were subsequently heated at 550°C for 2 and 4 hours. Some damage of the ZrN coating was observed due to the fuel-plate-fabrication process.

Irradiation experiments using ions and neutrons have been performed on samples from as-fabricated fuel that contain U-7Mo particles coated with 1 µm-thick ZrN. For the ion irradiation experiments, 80 MeV iodine ions were used to simulate in-reactor behavior.[15]. It was observed that in locations where cracks were present in the ZrN, extensive interaction occurred between the U-7Mo and Al matrix. However, where the ZrN coating was intact, no interaction was observed. To test the irradiation performance of ZrN coating using neutrons, a reactor test was performed using an Al matrix pin-type fuel and U-9Mo powders coated with 2–3 µm-thick ZrN.[16] It was observed that for burnups up to 60 and 84%, no U-9Mo/Al interaction occurred for locations where the ZrN coating was intact. Another reactor experiment that was performed used plate-type fuel and U-7Mo particles coated with 1-µm-thick ZrN, and it was performed in the BR-2 reactor as part of the Surface Engineering of Low ENriched Uranium-Molybdenum (SELENIUM) test.[13,12,17] The initial non-destructive examination (NDE) results that have been reported for this irradiation showed that the plate with ZrN-coated U-7Mo plates did not exhibit failure.

In order to further the understanding of the effectiveness of using a thin 1 µm-thick ZrN thin film as a diffusion barrier, where the film is deposited on U-7Mo particles using a STEPS&DRUMS process, it is useful to utilize multiple microstructural characterization techniques, including transmission electron microscopy (TEM). Detailed microstructural information, particularly at a low-length scale, can help in determining the effects of irradiation during subsequent reactor testing. To this end, U-7Mo fuel particles with a 1-µm-thick ZrN coating deposited using the same barrel coating system as those that were tested in the SELENIUM reactor test have been characterized using scanning electron microscopy (SEM) and TEM. The samples for characterization were produced from fuel plates with Al-6061 (AA6061) cladding that were fabricated at 500°C. The

main difference between the ZrN coatings discussed in this paper and those that were irradiated in SELENIUM is that the SELENIUM plates were fabricated at a temperature no higher than 450°C.[15] It is beneficial to characterize samples from fuel plates fabricated at a higher temperature to investigate the effect of the relatively high temperature fabrication process on the ZrN coating. This paper discusses the results of the microstructural characterization that was performed and compares the observed microstructural features with what has been described in the literature for IV–B transition-metal nitride coatings deposited using low-temperature PVD techniques. Comments will be made on how the observed ZrN microstructure may impact its use as a diffusion barrier.

2 Materials and Methods

The starting U-7Mo powders were provided by personnel at the Korean Atomic Energy Research Institute (KAERI). The powders were produced via centrifugal atomization [Ki Hwan Kim, Don Bac Lee, Chang Kyu Kim, Gerard E. Hofman, Kyng Wook Paik, "Characterization of U-2 wt% Mo and U-10 wt% Mo alloy powders prepared by centrifugal atomization," J. Nucl. Mater. 245 (1997) 179-184]. A 1- μm -thick ZrN coating was applied to the U-7Mo powders (mean particle size of 70 μm) in the as-received condition with no pre-treatment of the powder surface by personnel at the Studiecentrum voor Kernenergie, Centre de l'Energie Nucléaire (SCK–CEN) in Belgium. The STEPS&DRUMS system described earlier was employed to complete the process. The following are the steps of operation that were used: (1) attach a high-purity Zr target; (2) operate the source at a power of 800 W; (3) pump down the reactor to around 10^{-6} mbar; (4) admit high-purity argon gas into the chamber at a rate of 80 cc per minute; (5) add high-purity nitrogen at a rate of 6 cc per minute while reducing the Ar flow to 76 cc; and (6) rotate the drum at around 2–5 rotations per minute. The total sputter time can be up to 7 hours.[13] The use of a high-purity Zr target and high-purity argon and nitrogen gas were employed to mitigate the impurity content in the produced ZrN coating.

A U–Mo dispersion fuel plate was fabricated for ultimate destructive examination using ZrN-coated U-7Mo particles following standard steps.[18] In short, the ZrN-coated U-7Mo fuel powder received from SCK–CEN was blended with Al powder—in which the major impurities were 0.09 wt.% Fe and 0.03 wt.% Si—and pressed into a compact, where the ZrN-coated U-7Mo particles made up approximately 50 volume percent. The compact was placed in an AA6061 picture frame, sandwiched between AA6061 cover-plates, roll-bonded at 500°C to final thickness, and sheared to final plate length [18]. The final fuel loading of the fuel plate was 8 grams U/cm³.

From the as-fabricated fuel plate, transverse and longitudinal cross sections were sliced using a slow-speed saw. The cross sections were mounted in epoxy, metallographically polished, and then characterized at the Microscopy and Characterization Suite (MaCS), Center for Advanced Energy Studies (CAES) at Idaho National Laboratory (INL). A scanning electron microscope was used to produce both secondary electron images (SEIs) and backscattered electron images (BEIs) of the microstructure. Compositional analysis was performed using energy dispersive spectroscopy (EDS). Samples were produced for TEM using a focused ion beam (FIB) in situ lift out (INLO) technique similar to that discussed in Reference [D. D. Keiser, Jr., Brandon Miller, James Madden, Jan-Fong Jue, and Jian Gan, "Nano-Scale Fission Product Phases in an Irradiated U-7Mo Alloy Nuclear Fuel" *Microscopy Today*, 22(5)

(2014) 30-34]. The TEM analysis was performed in a FEI Tecnai G2 F30 STEM, equipped with a high-angle annular dark field (HAADF) detector. For each specimen, both low- and high-magnification Bright Field (BF) and HAADF STEM images were collected for bulk and detailed analysis. Selected area and convergent-beam diffraction patterns (SAED and CBED) were collected and indexed to crystallographically identify the phase constituents. Standard TEM BF micrographs were produced to characterize the microstructure. HAADF micrographs were used to identify compositional contrast. EDS was employed to determine phase composition.

3 Results

3.1 Scanning Electron Microscopy

A dispersion fuel plate was fabricated using ZrN-coated U-7Mo particles. A uniform distribution of the fuel particles was observed throughout the plate as shown in the BEI in Figure 1(a). Thinning of the end of the fuel zone region in the rolling direction (longitudinal view), referred to as dog-boning, was observed and is shown in Figure 1(b). No deformation was observed in the width of the fuel meat region (transverse view).

The arrows in Figure 1 (a-c) mark fine particulate observed within the Al-matrix that appears to be loose ZrN particles. Some ZrN overspray is produced during coating of the fuel particles, and the ZrN particulate ends up mixed with the ZrN-coated U-Mo particles when this material is not removed via sieving. Some of this material could also be ZrN coating that has broken away from the fuel particles during fuel plate manufacturing.

In general, two different coating microstructures developed on the fuel particles. Figure 2(a) shows the most common microstructure, where fuel particles developed uniform or nearly uniform coating. The coatings on these particles successfully prevented U-Mo interactions with the Al-matrix. On particles where the coating was fractured or not present, significant interactions were observed. Figure 2(a) also shows the cored microstructure of a U-7Mo fuel particle produced by centrifugal atomization, where at cell boundaries the Mo content is around 2-3 wt.% lower than the cell interiors [A. Leenaers, S. Van den Berghe, E. Koonen, C. Jarousse, F. Huet, M. Trobas, M. Boyard, S. Guillot, L. Sannen, and M. Verwerft, "Post-irradiation examination of uranium-7 wt% molybdenum atomized dispersion fuel," J. Nucl. Mater. 335 (2004) 39-47.]. This microstructure did not appear to result in unique reaction regions with the ZrN in areas with lower Mo content. Figure 2(b) shows a fuel particle with a fractured coating and fractured U-Mo/Al interaction layer. A significant interaction region developed within the U-Mo particle. Figure 2(c) shows that particle morphologies appear to have been modified during fuel plate manufacturing. Particles that have come into contact have been significantly deformed. Figure 2(d) confirms the fact that in most cases the ZrN appeared as a uniform coating around the U-7Mo particles.

Close examination of the microstructures of the ZrN-coating typically revealed what appeared to be an interface or a thin phase region near the middle of the coating as shown in Figure 3. The SEM lacked the resolution to discern any microstructural details of this feature. This feature may be tied to any original oxide layer that was present on the starting powder before any ZrN coating was applied. This region of the coating presented a focus area for subsequent TEM analysis.

Sample preparation by FIB revealed significant gaps between some ZrN-coated U-Mo particles and the Al-matrix, which is also observed for dispersion fuel without ZrN coating [T. C. Wiencek and I. G. Prokofiev, "Low Enriched Uranium-Molybdenum Fuel Plate Development," Paper published in the Proceedings of the 2000 International Meeting on Reduced Enrichment for Research and Test Reactors, Las Vegas, NV, October 1-6, 2000]. Figures 4 (a) and (b) show two

instances where lack of bonding between the ZrN-coated U-Mo particles and the matrix was observed. The mechanism that resulted in the occurrence of these voids was not considered in this study, but the void regions likely persisted during consolidation and compaction of the fuel particles with the Al powder to develop the fuel matrix.

3.2 Transmission Electron Microscopy

A total of five samples were prepared by FIB for STEM analysis. The samples were obtained from ZrN-coated U-7Mo that developed intact or near intact coatings. Four samples were parallel to the growth direction of the thin film, and one was obtained perpendicular to the direction of growth as shown in the schematics and SEI in Figures 5(a) and (b), respectively.

3.2.1 Samples Parallel to the Growth Direction

High angle annular dark field (HAADF) STEM micrographs of the four samples prepared in the direction parallel to the growth direction of the ZrN coating are shown in Figure 6. The ZrN layers on the four U-Mo particles developed similar microstructures containing columnar microstructures typical of PVD coating deposition. Two layers were apparent within the coatings. Based on Z contrast in the HAADF micrographs in Figure 6 and detailed in Figure 7, the first layer, Layer 1, was marked by a light gray region in the coating near the U-7Mo, where the columns appeared densely packed and the columnar boundaries were nearly evenly spaced. The second layer, Layer 2, developed columnar boundaries with a coarser morphology, with coarsening increasing in the direction of growth. A dark band marked the boundary between the two layers. It coincided with the interface observed in the SEM micrographs shown in Figure 3. The thickness of the coatings was relatively constant in any given particle. A difference in thickness was observed between coatings of different particles. The average coating thickness ranged from approximately 1.5 to 0.8 μm .

Porosity was observed at the interface between the coating and the Al matrix, as indicated in Figures 6 and 7. This seems consistent with the porosity observed in the SEM micrograph shown in Figure 4. Layer 2 showed significant porosity at the columnar boundaries, as can be observed in Figures 6 (a-d) and Figure 7. Figure 7 shows that the dark band that developed at the interface between layers typically followed the morphology of the U-7Mo particle, and it may indicate some diffusion could have occurred during fuel plate fabrication. It does not appear to be an independent phase region.

Z contrast may indicate a difference in composition of the columns in this region rather than the development of a different phase. Figure 7 shows that a continuous interaction layer appears to have developed at the interface between the U-7Mo and the ZrN coating. Also, based on Z contrast, dark gray precipitates developed near the interface in the U-7Mo alloy. In contrast, the interface between the Al and the coating in the samples analyzed by STEM did not show indications of an interaction layer between the Al and the ZrN. The possibility exists that Al/ZrN interactions took place in regions that were not analyzed by TEM. Based on the lack of bulk interdiffusion, the bonding that occurred between the Al and ZrN during fuel plate fabrication may be of a mechanical, rather than a metallurgical nature. This type of bonding may have limited Al/ZrN interactions. The effects of any oxide layers that may be present should also be considered. Figure 8 shows that some precipitates may have developed in the Al away from the interface between the Al and the coating, and they may have formed due to Al/ZrN interdiffusion along grain boundaries. The precipitates appear to be located at the triple junctions

between Al-grains, and the grain boundaries leading from these precipitates to the coating interface appear to be of brighter contrast suggesting a unique composition. Reliable EDS or diffraction data was not collected to positively identify the nature of these precipitates. This information is necessary to ensure that this material is not in fact ZrN or some other impurity in the Al matrix.

Figure 9 shows typical EDS compositional analysis of (a) Layers 1, (b) Layer 2, and (c) the interfacial band separating the layers in Figure 7. The compositions were measured at several locations on each of the particles analyzed by TEM. All the samples showed the very similar compositions. Based on the relative peak intensities, the coating had consistent nitrogen and zirconium concentrations. The EDS patterns show that oxygen was present in the coating. Layer 1 showed relatively low concentration of oxygen. The dark band that separated the layers showed an intermediate oxygen concentration. Layer 2 showed the highest oxygen concentration. The EDS patterns did not show any concentrations of Al, Mo or U, indicating that these elements did not penetrate into the coating. Figure 9 (d) shows that the interaction layer at the ZrM/U-7Mo interface was enriched with U and Zr, possibly UZr_2 , and contained some N and O. Figure 9 (e) shows that the dark precipitates in the U-7Mo near the interface contained U and O.

SAED patterns were generated by TEM from several individual grains and from selected regions that included large number of grains within the coating. Figure 10 shows one grain that was selected for diffraction analysis. This grain represents the typical grain size observed in the coating. Figures 10 (b-c) show three diffraction patterns that confirm the presence of the cubic-ZrN phase (cF8) in the coating. Figure 11 (a-b) show ring patterns generated from selected large regions of Layer 1 and Layer 2, respectively. These patterns revealed only the cubic-ZrN phase (cF8) throughout the coating. None of the SAED patterns from the low and high-oxygen containing regions showed any evidence of ZrO_2 , indicating that the oxygen may be in solid solution with the ZrN phase. Figures 12 (a-c) show diffraction patterns from the dark gray phase observed in the U-7Mo near the ZrN/U-7Mo interface. These patterns show that UO_2 (cF12) was present in the U-7Mo alloy, and the presence of this phase on the surface of U-7Mo powder will impact the nucleation and growth of the ZrN coating.

3.2.2 Sample Perpendicular to Growth Direction

One sample was produced oriented perpendicular to the growth direction of the ZrN to capture the transverse cross-section of the columnar ZrN microstructure, as shown in the schematic in Figure 5 (b). The sample was obtained very near the top, radially, of the particle to capture the columnar cross-section while minimizing the effect of the curvature of the particle, but it was obtained so that, because of the curvature, the sample cut through the thickness of the coating to capture the change in the columnar morphology as a function of the depth of the coating. Figure 13 (a) shows a HAADF micrograph of the sample that was produced. Figure 13 (b) shows the near-transverse cross-section of the coating. The arrow points in the direction of increasing depth in the coating. As the coating depth increases, the columns decrease in width, in agreement with the longitudinal view in Figure 6 (a-d). Generally the coating density increased, with a respective decrease in the size of the columnar boundaries.

Figures 14 (a) and (b) show a detailed HAADF and a bright field micrograph of the same region, respectively, of the transverse cross-section of the columns near the Al alloy. A very fine grained microstructure is observed within the columns containing grains tens of nanometers in size. This suggests that the grain-boundary area is very high in the coating,

and the effects of grain-boundary diffusion should be considered when accounting for the effectiveness of the ZrN as a diffusion barrier. The columnar boundaries microstructures appear black and white in the HAADF and bright field micrographs, respectively. Figure 14 (c) shows a detailed bright field micrograph of a columnar boundary. A lattice is present in the boundary area, indicating that the columnar boundaries may not be void regions. Figures 15 (a-d) show the typical compositions of the grains and the columnar boundaries near the Al and the U-7Mo. Comparison of the integrated intensities in Figures 15 (a) and (b) show that the grains in the coating contained some oxygen. Those near the Al contained a slightly higher oxygen concentration. Figures 15 (c) and (d) show that the columnar boundaries near the Al contained a significantly higher oxygen concentration than the boundaries near the U-7Mo. Figure 15 (c) shows that some Al was detected in the columnar boundaries near the Al, and none was observed near the U-7Mo. Some Al may have diffused into the coating through the columnar boundaries. However, the presence of Al may be the result of sample preparation and the rough microstructure of the coating near the Al. Peaks and valleys developed on the coating surface, as shown in Figure 15 (e), and the valleys typically developed at the columnar boundaries. Where the coating was in contact with the Al, the valleys were filled with Al. The sample may have intercepted some of the valleys containing Al, resulting in the identification of Al by EDS.

4 Discussion

4.1 Microstructural Features Expected for Thin Films Produced using Low Temperature PVD

The microstructural development of thin films deposited through PVD has undergone extensive studies [5, 6, 19-25]. The growth of a ZrN thin film during low temperature PVD deposition will go through the following stages: (1) the birth of the film, which starts with a random nucleation process followed by nucleation and growth stages; and (2) nucleation and growth stages that are dependent upon various deposition conditions, such as growth temperature, growth rate, and substrate chemistry. The film microstructure, associated defect structure, and film stress depend on the deposition conditions at the nucleation stage. The basic properties of a thin film, such as film composition, crystal phase and orientation, film thickness, and microstructure are also controlled by the deposition conditions [6].

Sputter deposition results in columnar growth, which Thornton describes as a "fundamental consequence of forming a solid from a vapor flux [arriving] from one direction"[5]. Many reports of columnar microstructure have appeared in the literature [20]. This structure has been observed by microfractography, TEM, small-angle electron and x-ray scattering. The effect of this structure on the physical properties of the film material is often remarkable. The surface topography, specific surface area, oxygen uptake and adhesion to the substrate are affected by the existence of the columnar structure.

Movchan and Demchisin have developed a structure zone diagram (SZD) to describe the microstructural development (during evaporation) as a function of the film growth temperature (T/T_m), where T is the substrate temperature and T_m is the melting point of the material [19]. Based on the diagram provided by Movchan et al., three temperature zones can be distinguished. Zone 1 is at a T/T_m ratio <0.3 . In this zone, the adatom mobility is low, leading to continuous nucleation of grains. This results in a fine-grained structure of textured and fibrous grains. The grains point in the direction of the arriving

vapor flux and end with domed tops. For Zone 2 ($0.3 < T < 0.5$), surface diffusion sets in, leading to uniform columnar grains. The grain size increases with T/T_m and may extend all the way throughout the film thickness. The surface ends of the grains lead to a faceted surface. For Zone 3, at $T/T_m > 0.5$ bulk diffusion and recrystallization leads to dense films with large grains.

The ZrN coating in this study developed the expected columnar microstructures, due to the fact that the ZrN, with a T_m of around 2950°C, was deposited at room temperature. Based on the Movchan et al. SZD, the coatings deposited in this study were within the Zone 1 regime. The coating developed the expected thin columns with very fine grained microstructures, and significant open voids between the columns, as can be observed in Figures 10 (a) and 14.

4.2 Important Characteristics for a Thin Film Diffusion Barrier

In the dispersion fuels under consideration, U-Mo alloy fuel particles are embedded in an Al-matrix, which provides structural support to the fuel meat. The diffusion barrier coating serves the purpose of separating U-Mo particles from the Al-matrix to eliminate detrimental diffusional interactions that take place between the matrix and the fuel during fuel system fabrication and under irradiation. In order to use a thin-film as a diffusion barrier to eliminate such interactions, it is important that the optimal attributes of such a barrier be understood. Nicolet has identified the conditions that need to be met for a material to be a good diffusion barrier [10]. For a case where diffusion barrier "X" is placed between material "A" and "B," the transport of A across X and of B across X should be small. The loss rate of X into A and of X into B should be small. X should be thermodynamically stable against A and against B, and there should be strong adhesion of X with A and with B. X should be laterally uniform in thickness and structure. X should be resistant to mechanical stress and thermal stress, and X should be highly thermally conductive. X should be compatible with steps employed during fabrication, and there needs to be the capability to deposit X reproducibly with existing equipment. For the case of nuclear fuel systems' materials, stability of the barrier material under irradiation is also a critical factor.

As stated by Grigorov et al. [27], the performance of a barrier depends on structural (physical structure, structural defects) and chemical (metallurgical interactions) aspects. The physical properties of a material, such as the grain sizes, defects, texture, stress and other structural characteristics, generally control its mechanical performance. The method of fabrication typically controls the physical properties. Therefore, the procedure applied in the fabrication process of a diffusion barrier can be a critical factor in its success or failure.

4.3 Thermodynamic Stability

Thermal stability, as described by Hulman [28], is an important aspect for thin films. It is impacted by phase equilibrium, diffusion, recrystallization, interfacial reactions, and oxidation. Thermodynamic equilibrium is seldom achieved by thin-film deposition methods. A kinetic limitation induced by low-temperature deposition allows for synthesis of metastable phases. Diffraction analysis of the coatings in this study showed that the coatings were composed of the cubic-ZrN phase. Recrystallization can impact the thermal stability of a diffusion barrier [28]. The small grain size and large levels of compressive intrinsic stress typical for PVD films offer significant driving forces for recrystallization. The possibility exists that deposition initially resulted in the development of nonequilibrium

phases. The coating may have undergone recrystallization that resulted in the development of the thermodynamically stable cubic-ZrN phase. Because significant time elapsed between deposition and analysis time, a recrystallization mechanism was not confirmed and remains a source for further study.

Although nitrides are thermodynamically stable, they are readily oxidized even at room temperature [35-40, 4]. ZrN is considered to have poor oxidation resistance. Oxidation or contamination by oxygen can be a problem since it modifies the properties and reactivity of the material [35]. Alexandre et al. [36] performed a study of oxidation of ZrN between 550 and 700°C. A proposed mechanism involved the formation of zirconium-oxygen solutions that preceded the formation of zirconia, and the scale that formed on samples was non-protective. Krusin-Elbaum and Wittmer have studied oxidation of reactively sputtered ZrN in dry oxygen [37]. XRD analysis showed that a cubic phase of ZrO₂ and a monoclinic phase formed due to the reaction. These phases persisted up to the highest oxidation temperatures tested. Prieto et al. studied the oxidation of ZrN at room temperature [39]. They observed that at low oxygen exposures, ZrN was unaffected except for some oxygen adsorption on the surface. At larger oxygen exposure, ZrN_xO_y and ZrO₂ phases grew on the ZrN surface until a continuous oxidized layer was formed at saturation. Milosev et al. reported that ZrN oxidation up to 450°C results in the formation of oxynitride layers [40].

The ZrN coating in this study showed significant concentrations of oxygen at the columnar boundaries, as shown in the EDS patterns in Figure 15 (c) and (d). Individual grains near the Al showed some oxygen concentration, as shown in Figure 15 (a), and those near the U-7Mo showed negligible oxygen concentrations, as shown in Figure 15(b). The grains near the Al may have been exposed to air, prior to fabrication of the fuel plate, with enough time at room temperature for oxygen to penetrate the grain lattices. Because the grains near the U-7Mo contained little oxygen, the results also indicate that oxygen adsorption through the columnar boundaries only affected surfaces of the columns. After the fuel plates were fabricated, the ZrN coating may have been protected against further oxidation at room temperature by embedding it in the Al-matrix and isolating it from the environment.

4.4 Chemical Interactions and Coating Adhesion

The binary phase diagrams for Al-N and Al-Zr indicate that interactions between the ZrN coating and the Al-matrix can potentially take place. According to Krusin-Elbaum et al. [41], ZrN has been evaluated as a diffusion barrier in aluminum metallization schemes, requiring an assessment of its compatibility with Al and Si. ZrN films were annealed to test metallurgical interaction with Al, Si, and SiO₂ layers in a furnace flushed with purified He. For testing of interactions with Al and Si, a 330 nm-thick layer of Al was deposited on top of ZrN with a Si wafer as a substrate. A series of 30-minute anneals were performed at various temperatures. No interactions were observed in the generated RBS spectra until 550°C was reached. This indicated a reaction between Al and the ZrN film was initiated. From XRD analysis, Al₃Zr was found to have formed at the Al/ZrN interface. Further annealing at 600°C for 30 minutes showed complete failure of the ZrN such that a Si signal could be observed, and a Zr₃Al₄Si₅ compound was identified. It was concluded by the authors that failure of the ZrN as a diffusion barrier at higher temperatures was due to the decomposition of the ZrN by reaction with the Al. In the current study the development of an interaction regions between the Al and the

ZrN coating were not observed, suggesting that the fabrication techniques used to develop the dispersion in the Al-matrix did not achieve high enough temperatures for long enough times to initiate interactions between the coating and the Al. Interactions may have also been hindered by the significant porosity observed between the coating and the Al-matrix, as was shown in Figures 6 and 7. This porosity may have resulted in a relatively weak bond between the coating and the matrix that may be mechanical rather than chemical in nature. Compositions of the precipitates observed in the Al away from the interface are suspected to be composed of Zr. However, their nature was not confirmed in this study. Porosity at the interface between the coating and the matrix may not be desirable. During irradiation, gas fission products may accumulate within these pores, subsequently resulting in runaway swelling of the fuel plate.

The coating in this study interacted with the U-7Mo particles, as can be observed from Figure 7. The binary phase diagrams for Mo-N, Mo-Zr, U-N, and U-Zr indicate that there is a potential for U-7Mo to interact with the ZrN coating to form phases. Metallic Zr is another material being developed as a diffusion barrier for application in a LEU fuel. Instead of a dispersion fuel, the fuel is of a monolithic design where a U-Mo foil is encased in AA6061 cladding [42]. In this system, a 25- μm -thick Zr foil is placed between the fuel and the AA6061 cladding to serve as a barrier to eliminate unacceptable metallurgical interactions. Studies on this system have shown that the interaction layers that develop during manufacturing actually result in good adhesion of the Zr to the U-Mo alloy. The thickness of the interaction layers is relatively small, and the interaction products between Zr and U-Mo, based on reactor testing, are acceptable for reactor operation. Thus the ZrN coating, with an interaction zone at the U-7Mo/ZrN interface, may similarly serve as an acceptable diffusion barrier.

4.5 Radiation Stability

Ultimately, the radiation stability of a coating material is critical for its successful application in a nuclear fuel. ZrN has been evaluated for non-diffusion-barrier applications in nuclear fuels. One application under consideration for ZrN is the use of this material as an inert matrix in some types of nuclear fuels. To test the radiation stability of bulk ZrN, both proton- and ion-irradiation experiments have been performed [43, 44]. It has been observed that bulk ZrN is highly resistant to radiation-induced amorphization up to 800°C using 2.6 MeV protons [45]. In addition, bulk ZrN has been demonstrated to be tolerant to low-energy, heavy and light ion bombardment [46, 47]. Of particular interest for the current study is the response of a ZrN microstructure similar to what was observed for a ZrN coating deposited using a barrel deposition system. As described earlier, a fine-grained microstructure was observed in the current study, and so the results of ion beam irradiations of ZrN with this kind of microstructure is of interest. Nanostructured materials are suggested to have significantly improved stability against radiation damage, owing to the high density of interphases and surfaces that provide sinks for the annihilation of radiation-induced defects [48].

Lu et al. irradiated nanocrystalline ZrN on a Si substrate using 300KeV Ne and 1 MeV Kr [48]. Results showed that up to fluences of 0.4, 4, and 20 dpa, the isometric structure of ZrN was unchanged when exposed to 300 keV Ne ions. However, a unit cell contraction may have occurred (by 1.42%). In addition, irradiation using 350 keV oxygen ions seemed to cause the ZrN to contract (by ~0.99%). For the 1.46 GeV and 1.69 GeV Xe ion irradiations, the unit cell remained unchanged throughout the irradiations. Also,

through the experiments, the average grain size remained unchanged after the irradiations. A loss of nitrogen was observed by RBS measurements. The loss was linked to migration of displaced nitrogen interstitials to the grain boundaries and fast diffusion along the grain boundaries. The study determined that the nano-crystalline ZrN is resistant against radiation-induced growth. The ion irradiation results also suggested that nanocrystalline ZrN has a different response than bulk ZrN to ion irradiations with different energy-loss mechanisms.

Additional research by Janse van Vuuren et al. [49] reported the results of high-energy Xe, Kr, and Bi ion irradiations on the stability of ZrN coatings. The ZrN layers that were tested had a nanocrystalline microstructure (average crystallite size of 4 nm) and different thicknesses (0.1, 3, 10, and 20 mm). The coatings were produced using a vacuum arc vapor deposition method. Microstructural characterization of unirradiated and irradiated samples showed that the ZrN layers had the standard face centered cubic (fcc) structure of the NaCl-type with a {111} preferred orientation. No apparent changes in the phase composition of the layers were observed after irradiation. For the thinner samples irradiated with 167 MeV Xe ions, a relatively small decrease in the lattice parameter was observed for the 0.1 mm-thick sample, and a small increase was observed for the 3 mm-thick sample. The small increase for the 3 mm-thick sample was surmised to be due to accommodation of Xe impurities in the ZrN lattice. In the irradiated ZrN layers, there was no evidence of amorphization. XRD results showed no appreciable shift in the diffraction lines for ZrN, suggesting that any damage from the irradiation ions had no permanent effects. HRTEM results showed that the nanocrystalline nature of the ZrN layers was unaffected by irradiation for the 100 nm and thicker layers, even at the highest fluence. Hardness testing of the 3 mm-thick layers showed no appreciable effects due to radiation damage. Therefore, the results from XRD, TEM, and nano-indentation analysis showed that nanocrystalline layers are highly resistant to radiation damage effects associated with swift heavy ions of fission-fragment energies (i.e., greater than 100 MeV).

As described earlier in this paper, Jungwirth et al. [15] also performed ion irradiations on samples containing U-7Mo fuel particles with 1 μm -thick ZrN coatings. These coatings were deposited on U-7Mo fuel particles using the same STEPS&DRUMS process as the samples characterized in this paper. After ion irradiations were performed using 80 MeV iodine ions, it was determined that no interaction was observed between the U-Mo and Al due to the ion-irradiation process in regions where the ZrN thin film remained intact. This suggested that the ZrN was acting as a good diffusion barrier. Limited information about the radiation stability of ZrN was generated from this work. The emphasis was on studying the diffusion behavior of dissimilar materials during ion irradiation.

ZrN exhibits good radiation stability when exposed to light and heavy ions, as described above, but data from actual in-reactor experiments will be needed to more comprehensively determine the radiation stability of ZrN coatings. Microstructural characterization of U-7Mo dispersion fuel particles with PVD-deposited ZrN that were irradiated in the BR-2 reactor will provide some of this needed information [17].

4.6 Coating optimization to meet the important characteristics of a thin-film diffusion barrier for reactor service

Based on the results of SEM and TEM characterization of ZrN thin films deposited using the STEPS&DRUMS process, there is good agreement with the microstructural characteristics reported in the literature for high-melting-point PVD thin films deposited at low temperature: an as-deposited thin film that has fine, columnar grains. Relatively high porosity would be expected to form, and the observed presence of oxygen in the coating would not be unexpected.

With respect to the key attributes of an effective thin-film diffusion barrier (i.e., good thermal stability, good adhesion, low porosity, relatively large grain size, low stress, low oxygen contamination, good radiation stability, and negligible chemical interactions), the microstructural characteristics for the ZrN discussed in this paper suggest that changes could possibly be made to improve the diffusion barrier attributes, if needed, based on reactor testing observations. Some examples of possible improvements include:

(1) increasing the grain size in order to reduce the grain boundary area present in the thin film that could lead to an increase in diffusion rates; (2) reducing the oxygen content, so that the majority of the thin film is the intended ZrN; (3) increasing the density of the ZrN to make the thin film potentially more impervious to fuel constituents and fission products; and (4) improving the adhesion of the thin film at the interface with Al (i.e., less porosity and better contact) to improve the overall integrity of the fuel system. For a nuclear-fuel application, the ZrN thin film is intended to act as a diffusion barrier; the goal is to reduce or eliminate the interaction of the U-7Mo fuel particle with the Al matrix and to mitigate or eliminate the transport of fission products (gases or solids) to the Al/ZrN interface during irradiation. Further research is necessary to identify the key microstructural attributes that will be required for achieving the optimal ZrN thin-film diffusion barrier in an irradiated U-7Mo dispersion fuel.

5 Conclusions

Based on the SEM/TEM characterization of a ZrN thin-film diffusion barrier applied onto U-7Mo powders using low-temperature PVD and then exposed to U-7Mo dispersion fuel plate fabrication conditions, the following conclusions can be drawn:

- The ZrN thin film exhibits a columnar microstructure where the boundaries of the columns appear to be more porous than the regions at the center of the columns, and the coating microstructure coarsens near the ZrN/Al interface resulting in a region with the highest relative porosity.
- Relatively high levels of oxygen can be observed in the ZrN extending from near the ZrN/Al interface towards the U-7Mo. Oxygen concentrations were highest within the columnar boundaries. The grains within the columns contained low to negligible oxygen concentrations. It is unclear whether the oxygen was present in the as-received coated powder or penetrated into the ZrN during fabrication.
- Limited interactions of ZrN and Al took place. The bond between the coating and matrix in as-fabricated U-7Mo dispersion fuel could be mechanical in nature. The manufacturing process temperature or the high porosity at the Al/ZrN interface may have impacted the quality of the bond.
- An interaction zone between the U-7Mo and ZrN was observed. The phases in this zone are extremely small and may contain U in combination with the impurities carbon, nitrogen, and/or oxygen.
- Very fine-grained microstructures were observed in the coatings with grains that were

tens of nanometers in size, resulting in the presence of a high fraction of grain boundaries that could serve as fast diffusion paths.

- Diffraction analysis showed that the cubic-ZrN phase (cF8) was the only phase that developed within the coating.

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Figure captions

Figure 1. BEI of the bulk microstructure of the fuel plate. (a) Typical microstructure of the bulk of the plate. (b) Longitudinal view showing thinning at the edge of the fuel zone region in the rolling direction. (c) Transverse view showing a deformation free edge of the fuel meat.

Figure 2. BEIs showing (a-b) the morphologies observed for the ZrN-coated fuel particles. (c) A BEI showing a more general aspect of the fuel plate microstructure where fuel particles (highlighted by ellipses) that are in contact can become deformed during fuel plate fabrication. (d) Secondary electron micrograph of particles with nearly ideal coatings of uniform thickness, similar to (a).

Figure 3. BEI showing an interface near the center of the ZrN thin film that separates regions with two different grain morphologies.

Figure 4. SEM images of region where a FIB was used to generate a trench that extended into the sample and exposed the ZrN/Al interface for a particle similar to the one shown in Figure 3c. Significant voids are observed between the ZrN-coating and the Al-matrix.

Figure 5. Schematic diagrams showing where a FIB sample is sliced through the ZrN to capture samples that exposed the microstructure (a) parallel and (b) perpendicular to the growth direction.

Figure 6. HAADF micrographs showing the similarities of the ZrN-coating microstructures observed in the four samples prepared perpendicular to the growth

direction. (a) sample 1, (b) Sample 2, (c) sample 3, and (d) sample 4.

Figure 7. HAADF micrograph showing typical ZrN-coating microstructural features. Based on microstructure, the ZrN layer can be divided into high and low oxygen concentration regions separated by a dark band. Porosity is observed at the Al/coating interface. An interaction region developed at the U-7Mo/coating interface that contained U-Zr enriched phases and UO_2 .

Figure 8. High-magnification HAADF micrograph showing the presence of precipitates in the Al matrix. Grain boundary diffusion of ZrN constituents may have caused the development of some of these precipitates. Porosity, typical of the interface between the Al and the coating is also present in the image.

Figure 9. Typical EDS compositional analysis of (a) Layers 1, (b) Layer 2, and (c) the interfacial band separating the layers in Figure 7. (d) The composition of the interaction layer at the ZrN/U-7Mo interface was enriched with U and Zr, possibly UZr_2 , and contained some C, N and O. (e) the composition of the dark precipitates in the U-7Mo near the interface showing C, U and O.

Figure 10. (a) High magnification bright field micrograph of a single grain within the ZrN-coating. (b-c) electron diffraction patterns confirming the presence of the cubic-ZrN (cF8) phase.

Figure 11. SAED patterns for (a) the low and (b) high oxygen layers depicted in Figure 7. Based on the observed rings and the large number of grains captured, the cubic-ZrN (cF8) phase is comprised of very fine grains. Zr-O phases were not detected.

Figure 12. Electron diffraction patterns generated from a grain within the dark contrast phase observed near the interface between the ZrN-coating and the U-7Mo alloy. The patterns confirm the presence of the UO_2 (cF12) phase.

Figure 13. HAADF micrographs showing the microstructure observed for a sample oriented nearly perpendicular to the ZrN growth direction. (a) shows the complete sample, and (b) shows a selected region. The sample was prepared so that the full depth of the coating was captured. The arrow points in the direction of increasing depth.

Figure 14. (a) Detailed top view HAADF micrograph of a section of the coating near the Al-interface. (b) A bright field micrograph of the same region detailing the grains within each column. (c) A bright field micrograph of the columnar boundary marked in (b) detailing the presence of a lattice in the columnar boundaries.

Figure 15. EDS spectra detailing the variation in oxygen concentration of (a) a grain within a column near the Al-interface and (b) a grain near the U-7Mo interface, (c) a columnar boundary near the Al-interface, and (d) a columnar boundary near the U-7Mo interface. (d) is an SEI showing the non-uniform surface (arrow) of the ZrN coating.

Images to:

Microstructural Characterization of a Thin Film ZrN
Diffusion Barrier in an As-Fabricated U-7Mo/Al
Matrix Dispersion Fuel Plate

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15