Advanced Damage-Tolerant Ceramics: *Candidates for Nuclear Structural Applications*

Michel W. Barsoum – Drexel University – barsoumw@drexel.edu

The MAX phases, a class of machinable, layered, ternary carbides, and nitrides, have great promise for use in the next-generation of nuclear reactors. This is the first time the MAX phases have been neutron irradiated at temperatures as high as those carried out here.

This project is a collaborative effort between the Idaho National Laboratory (INL), Savannah River National Laboratory, and Drexel University aiming to explore the neutron irradiation response of MAX phases (i.e., Ti_3SiC_2 and Ti_3AlC_2) for advanced nuclear applications. Samples of each composition were irradiated in the Advanced Test Reactor (ATR), with nominal irradiation conditions of 0.1, 1, and 9 dpa at 100, 500, and 1000°C. Post-irradiation examination was performed at the Center for Advanced Energy Studies, including X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and resistivity testing.

Project Description

Robust materials are critical to meet evolving advanced reactor and fuel designs. These materials need to operate in extreme environments of elevated temperatures, corrosive media, and high-radiation fluences, with lifetime expectation of greater than 60 years. Full understanding of a material's response to irradiation is paramount to long-term, reliable service. The layered ternary carbides and nitrides, known as MAX phases, have the potential to be used in the next-generation nuclear reactors. All MAX phases are fully machinable even though some of them, such as Ti_3SiC_2 and Ti_3AlC_2, are similar to titanium metal in density, but are three times as stiff. The thermal and electrical conductivities are high and metal-like. They have relatively high-fracture toughness values and some are chemically stable in corrosive environments. They also have shown irradiation damage tolerance in heavy ion studies.

The aim of this project is to investigate the damage in Ti_3SiC_2, Ti_3AlC_2, and chemical vapor deposition SiC (for comparison) after exposure to a spectrum of neutron irradiations consistent with conditions found in light water nuclear reactors. The carbides are exposed to a series of neutron fluence levels (0.1, 1, and 9 dpa) at moderate to high irradiation temperatures (100, 500, and 1000°C) in the ATR at INL. The damage to the microstructures and the effects of the radiation on the mechanical and

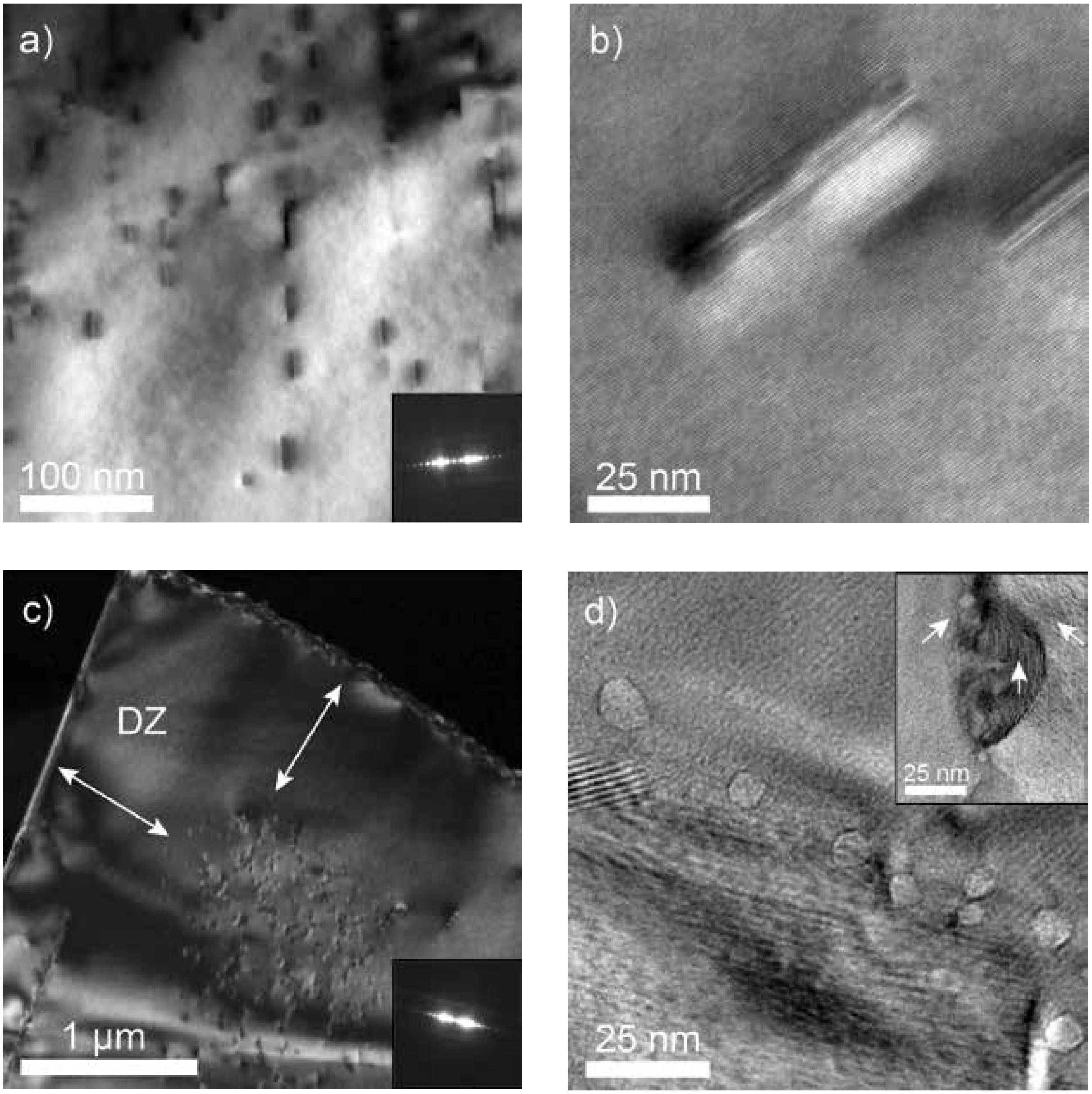

Figure 1. Brightfield TEM micrographs of Ti_3SiC_2 irradiated to 9 dpa at (a) 500°C showing dislocation loops imaged near the [11 $\bar{2}$0] zone axis, with an average loop diameter of 30(8) nm and a loop density of 2 x 1020 loops/m^3. (b) High resolution image of several loops in (a) exhibit a complex interaction of several loop stain fields arrayed along the c-axis. (c) Darkfield TEM micrographs of the same sample showing denuded zones, DZ (arrows), of 860(90) nm wide along both the a and c-lattice directions. (d) Brightfield micrograph showing spherical voids, which formed occasionally at the grain boundaries at this condition, with an average diameter of 7(2) nm. Inset of (d) shows small nanograins of Ti_3SiC_2 that were observed at the boundaries, which grew in different orientations to either parent grains (white arrows denoting a-axis direction).

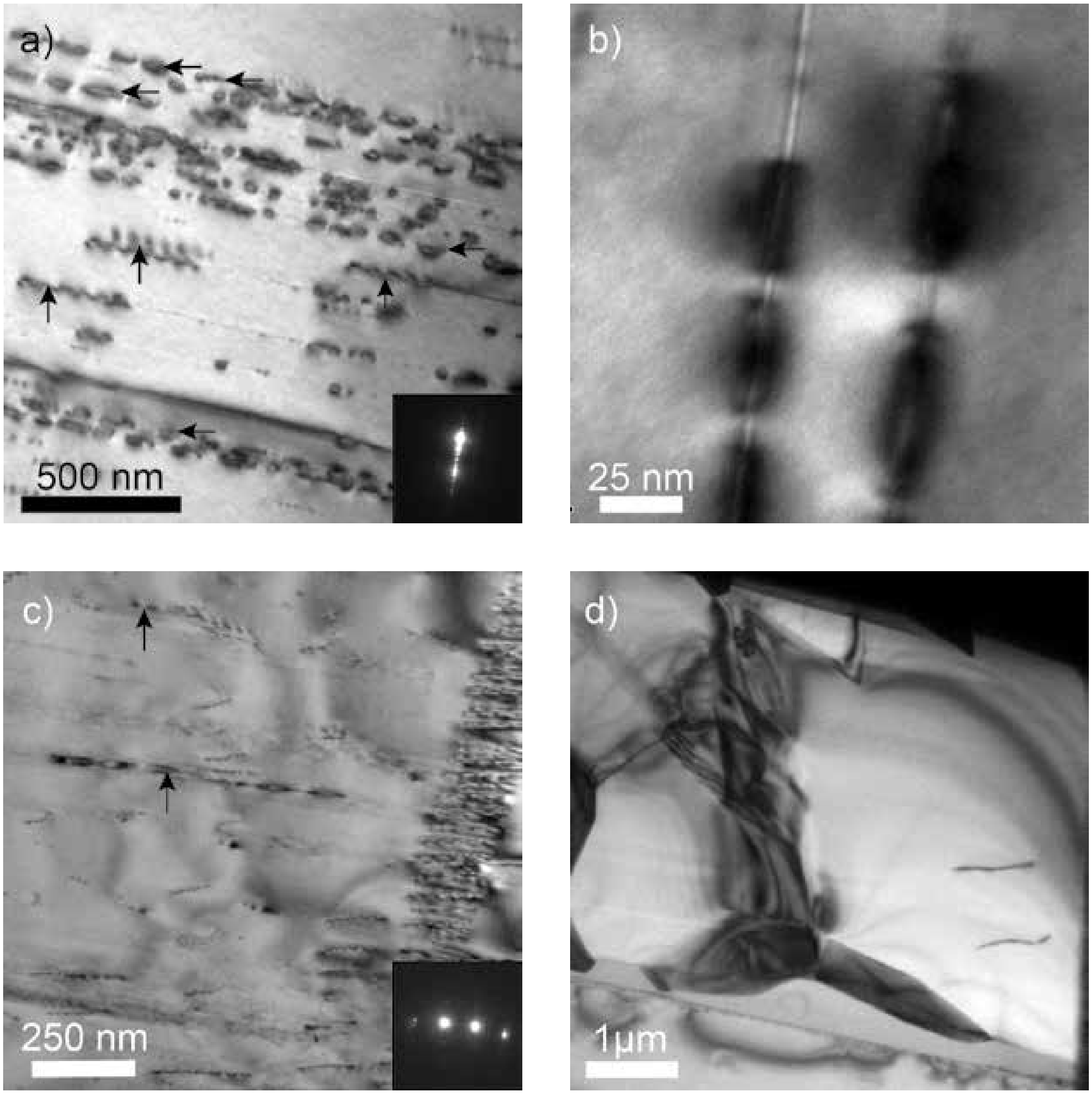

Figure 2. Bright Field TEM micrographs of Ti_3SiC_2 irradiated to 9 dpa at 1000°C reveal (a) basal dislocations (vertical arrows) and dislocation loops (horizontal arrows) pinned at stacking faults dispersed throughout a large grain, on average 63(25) nm in dia. with a density of 4 x 1019 loops/m³, only seen near stacking faults. (b) High-resolution micrographs of the loops in (a) reveal the c-axis strain contrast of the loop. (c) Tilting of this sample to g 1¯1 00 results in the loss of contrast for the b = ½ [0001] loops, while basal dislocations and arrays remain visible. (d) Smaller grains, and others without stacking faults, show no signs of irradiation induced dislocation loops.

electrical properties of the materials will be characterized during post-irradiation examinations. The results will provide an initial database that can be used to assess the micro-structural responses and mechanical performances of these ternaries.

Accomplishments

As of FY 2015, this project has been deemed completed. The irradiation of samples of Ti_3SiC_2 and Ti_3AlC_2 was conducted throughout the first two years of this project, which were then left to cool awaiting characterization. Due to unavoidable delays within the INL facilities, work on this project was delayed throughout FY 2013. In FY 2014, the receipt, cask unloading, experiment disassembly, and cataloguing of specimens were successfully accomplished, led by Collin Knight and Karen Wright. Upon examination, several samples were found to be fused together, notably in the 100°C capsules at higher irradiation conditions, and were unavailable for characterization. Work continued throughout FY 2014 and into FY 2015 as samples of Ti_3SiC_2 and Ti_3AlC_2, most desirably those irradiated to 9 dpa, became available for characterization.

Samples were mounted in metallographic epoxy to protect the workers from radiation exposure, and were first analyzed using XRD for phase and structure analysis. According to the Rietveld refinement of the XRD patterns collected, both Ti_3SiC_2 and Ti_3AlC_2 remained crystalline after irradiation, and both resulted in limited TiC formation. After irradiation at 100°C, a-LPs decreased and the c-LPs increased. Conversely, the lattice parameters of samples irradiated at all doses at 500 and 1000°C, were close to the pristine values, indicating that dynamic recovery was occurring at temperatures as low as 500°C.

With the collaboration of Lingfeng He at INL, extensive TEM work was conducted to explore the irradiation induced defects in Ti_3SiC_2 and Ti_3AlC. Dislocation loops with b = 1/2[0001] were observed in samples of Ti_3SiC_2 irradiated at 500°C, 21(6) nm dia. at 1 dpa, and 30(8) nm at 9 dpa (Figure 1a,b). In the Ti_3SiC_2 samples irradiated to 9 dpa, both at 500 and 1000°C, voids were observed within the grain boundaries (Figure 1d).

The MAX phases show great potential for irradiation damage tolerance due to their nanolayered structure.

— Darin J. Tallman, Ph.D. Research Assistant

Further, at 63(25) nm and 4 X 1019 loops/m^3, the largest loops in Ti_3SiC_2 were observed after irradiation to 9 dpa at 1000°C (Figure 2). However, these were only observed near stacking faults, and the majority of grains imaged showed no signs of irradiation damage in the bulk (Figure 2d). At 70(25) nm, the dislocations loops in Ti_3AlC_2 after irradiation to 9 dpa at 500°C were larger, and more numerous with a density of 8 X 1020 loops/m3 (Figure 3). Basal perturbations were also observed in Ti_3AlC_2 at these conditions (Figure 3d). TiC impurity particles were significantly more susceptible to irradiation damage, forming extensive defect clusters and dislocation loop networks (Figure 4).

Even more notable is the appearance of a large defect-free denuded zone, nearing 1 µm in size, in Ti_3SiC_2 irradiated to 9 dpa at 500°C (Figure 1c). Furthermore, at 1000°C, most grains on the order of 3–5 µm appear to be free of damage altogether (Figure 2d). This finding unequivocally demonstrates the ease of mobility of defects along the basal planes, and the lack thereof in the impurity particles.

These results confirm our initial conjecture that we postulated when we started this work. Namely, the A-layer in the MAX phases, sandwiched between hard M3 X 2 blocks, would provide stable defect accommodation sites, allowing for point defect accumulation, migration, and their ultimate annihilation. With increased irradiation temperature, the ease of migration along the basal planes allows for enhanced recovery of irradiation defects, resulting in the formation of coherent dislocation loops or annihilation of defects at the grain boundaries. The results from this work show that the MAX phases, notably Ti_3SiC_2, are able to withstand neutron irradiation damage, and recover from microstructural distortion with high-temperature irradiation. The project has thus provided the foundation for future experimental and theoretical studies for this promising family of materials for nuclear applications.

Future Activities

This project has concluded. No further work is expect to be performed. Samples will be transferred to the NSUF Sample Library and are available for future proposals.

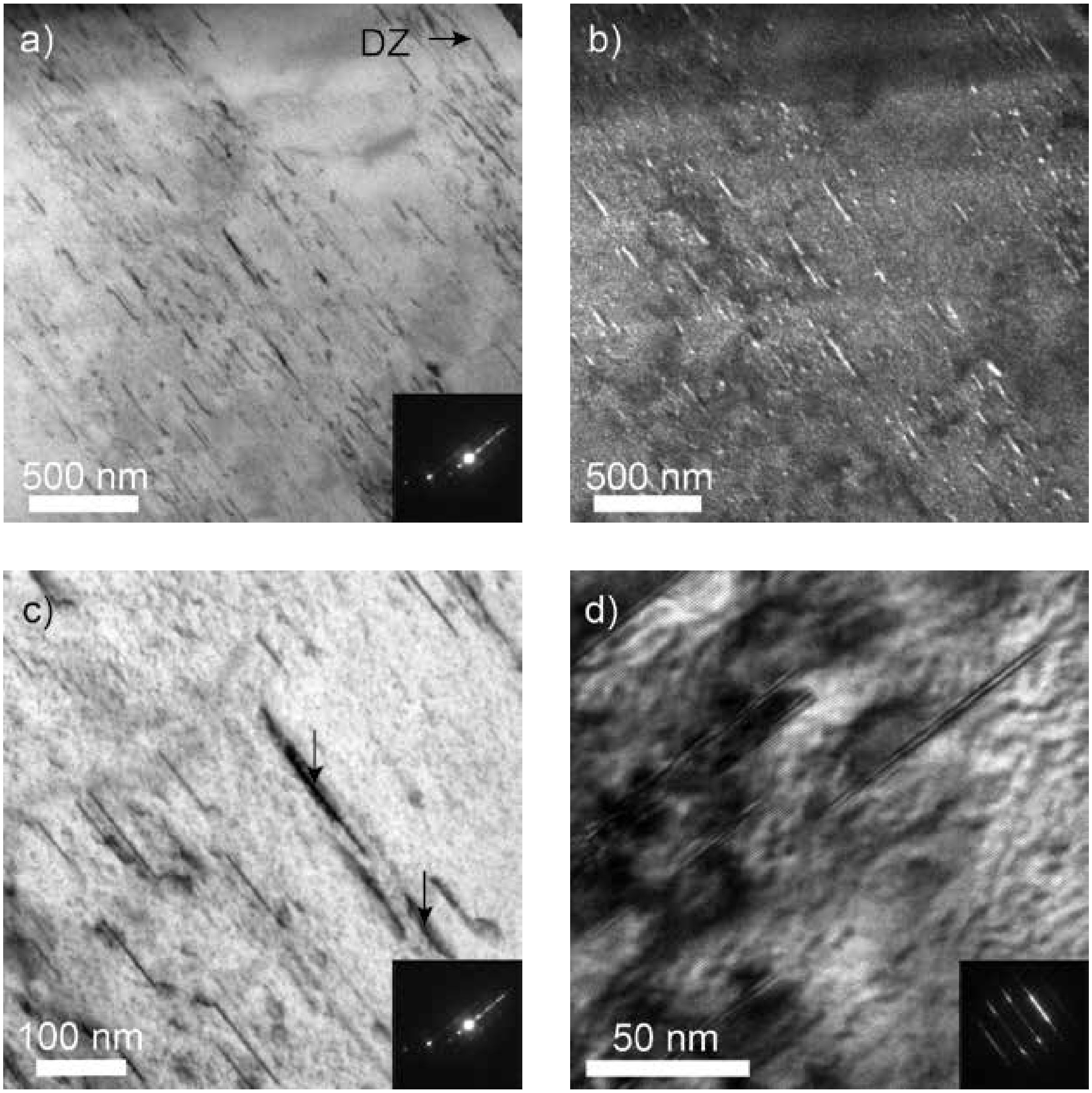

Figure 3. (a) Brightfield and (b) darkfield TEM micrographs of Ti_3SiC_2 irradiated to 9 dpa at 500°C showing dislocation loops and stacking faults imaged near the [11 $\bar{2}$0] zone axis with an average loop diameter of 70(25) nm and a loop density of 8 x 1020 loops/m^3. A denuded zone, DZ, of 140 nm can be seen at the grain boundary. (c) Higher magnification of a region in (a) reveals short stacking faults (black arrows), with a lack of Al content determined by EDS, and dislocation loops. (d) High-resolution micrographs of the loops in this region show extensive basal plane perturbation and loops within the basal planes.

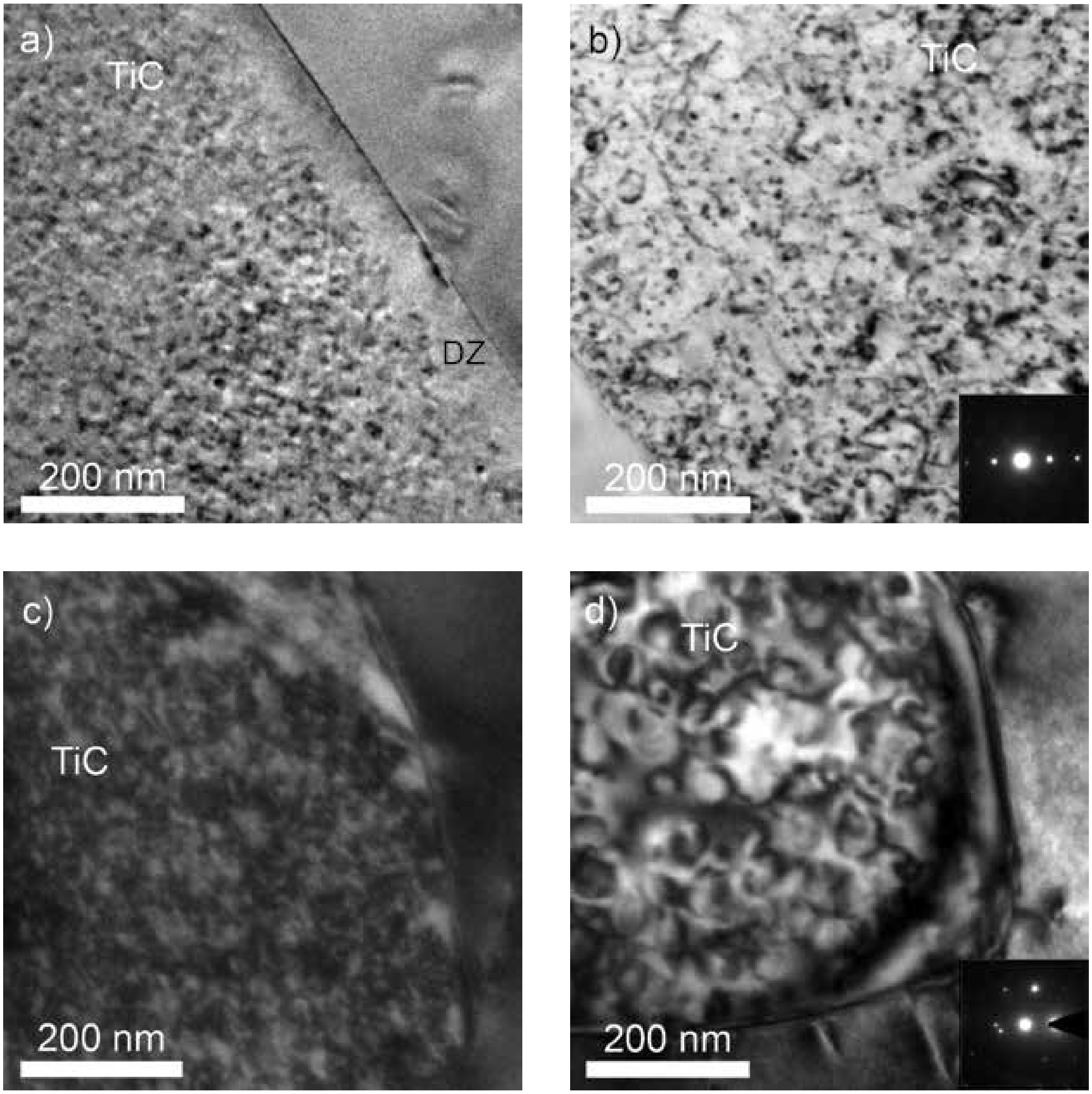

Figure 4. Brightfield TEM micrographs of TiC impurity particles in (a) Ti_3SiC_2 irradiated to 0.1 dpa at 1000°C, (b) 1dpa at 500°C, and (c) 9 dpa at 500°C, and (d) TiC in Ti_3AlC_2 irradiated to 0.1 dpa at 500°C. All TiC particles observed exhibited the formation of defect clusters and dislocation loops after irradiation, extensively more so than the surrounding MAX phase matrix.

Publications and Presentations*

1. Tallman, D. J., L. He, E. N. Hoffman, E. N. Caspi, B. L. Garcia-Diaz, G. Kohse, R. L. Sindelar, M. W. Barsoum, "Neutron Irradiation of MAX Phases," *Presented at Il Trovatore Meeting 2, Philadelphia, Pennsylvania, July 24, 2015.*

2. Tallman, D. J., L. He, E. N. Hoffman, E. N. Caspi, B. L. Garcia-Diaz, G. Kohse, R. L. Sindelar, M. W. Barsoum, "Nuclear Scientific User Facility: Neutron Irradiation of MAX Phases," *Presented at NSUF User's Week, Idaho Falls, Idaho, June 23, 2015.*

3. Tallman, D. J., L. He, G. Bentzel, E. N. Hoffman, B. L. Garcia-Diaz, G. Kohse, R. L. Sindelar, M. W. Barsoum, "Microstructural Defects in Neutron Irradiated Ti_3SiC_2 and Ti2AlC," *Presented at ICACC'15, Daytona Beach, Florida, January 28, 2015.*

4. Tallman, D. J., L. He, B. L. Garcia-Diaz, E. N. Hoffman, G. Kohse, R. L. Sindelar, M. W. Barsoum, Effect of neutron irradiation on defect evolution in Ti_3SiC_2 and Ti_2AlC, *Journal of Nuclear Materials, 468, 2016, pp. 1–13.*

5. Tallman, D. J., "On the potential of MAX phases for nuclear applications," Ph.D. Thesis, Drexel University, Philadelphia, Pennsylvania, 2015.

Distributed Partnership at a Glance

NSUF and Partners	Facilities and Capabilities
Center for Advanced Energy Studies	Microscopy and characterization Suite
Idaho National Laboratory	Advanced Test Reactor, Hot Fuel Examination Facility Analytical Laboratory
Massachusetts Institute of Technology	Nuclear Reactor Laboratory
Collaborators	
Drexel University	Michel Barsoum (principal investigator), Darin Tallman (collaborator)
Idaho National Laboratory	Jian Gan (principal investigator), Lingfeng He (collaborator)
Savannah River National Laboratory	Brenda L. Garcia-Diaz (collaborator), Elizabeth N. Hoffman (collaborator)