SAND2011-9349C

In situ TEM Ion Irradiation and Atmospheric Heating of Cladding Materials

K. Hattar[1], S. Rajasekhara[1], B.G. Clark[1]
[1] Sandia National Laboratories, Physical, Chemical, & Nano Sciences Center, PO Box 5800 Albuquerque, NM 87185, U.S.A.

ABSTRACT

Over the course of use, both in-service and during storage, fuel claddings for nuclear reactors undergo complex changes that can drastically change their material properties. Exposures to irradiation, temperature changes, and stresses, as well as contact with coolant, storage pool, and dry storage environments, may induce microstructural changes, such as formation of radiation defects, precipitate dissolution, and chemical segregation, that can ultimately result in failure of the cladding if pushed beyond its limit. In order to predict the performance of cladding in-service and during storage, understanding of the dominant processes related to these changes and their consequences is essential. *In situ* transmission electron microscopy (TEM) allows dynamic observation, at the nanoscale, of microstructural changes under a range of stimuli, making it an excellent tool for deepening our understanding of microstructural evolution in claddings. This proceeding presents details of the new *in situ* ion irradiation TEM and *in situ* gas cell TEM capabilities developed at Sandia National Laboratories. In addition, it will present the initial results from both systems investigating radiation tolerance of potential Generation IV cladding materials and understanding degradation mechanisms in Zr-based claddings of importance for dry storage.

INTRODUCTION

In order to identify suitable materials for next generation claddings and to certify performance of current cladding materials in-service and during subsequent storage, microstructural changes within the cladding and their impact on material properties must be well understood. In the case of Generation IV claddings, new reactor designs are directed at consuming harmful fission gasses for ease of reprocessing and lowering the safety risk in storage. However, to achieve this, fuel assemblies must endure much higher temperatures and irradiation damage than currently required in Generation II reactors. This has led to a push to evaluate new candidate materials for cladding, in particular searching for materials that can withstand greater than 100 dpa (displacements per atom), while still maintaining structural integrity. Another material degradation concern arises as Generation II fuel assemblies reach the end of their in-service specifications and are transferred to storage pools and subsequently dry storage casks. During this time, the cladding provides a barrier to the release of radioactive fuel material and fission gasses. To ensure that fuel assemblies are safe to be moved or transported in the future, the cladding must maintain its strength and ductility over potentially hundreds of years.

Currently, fundamental details of microstructural changes under these extreme environments in both Generation IV cladding material candidates and Generation II Zr-based alloys are lacking. Processes such as formation of radiation-induced defects and dissolution and reprecipitation of second phases, are not fully characterized as a function of material composition, grain structure, and environment. This gap in knowledge hinders the development of predictive models for certifying and determining the limits of cladding materials. To provide a physical foundation for the advancement of material models, experimental validation is crucial.

For the real-time study of fundamental microstructural changes in claddings, *in situ* transmission electron microscopy (TEM) is an invaluable tool. *In situ* TEM techniques were developed shortly after the invention of the TEM and continue to take advantage of the miniaturization of and advancements in microfluidics, microelectronics, and other manufacturing techniques [1]. This study will capitalize on recent developments in TEM stage design that permit the flow of atmospheric pressure air across a TEM sample within the 5 μm of an *in situ* TEM gas cell. Using *in situ* TEM gas cell experiments, formation, dissolution, and reprecipitation of embrittling second phases in Generation II claddingscan be studied. . In addition, the study will take advantage of the most recently developed *in situ* ion irradiation TEM to study the formation of radiation-induced defects of importance to the properties of Generation IV claddings as a function of irradiation dose [2]. Early results from both techniques are presented here.

EXPERIMENTAL PROCEDURE

An *in situ* ion irradiation TEM was developed at Sandia National Laboratories through the union of a 6 MV Tandem accelerator and a JEOL 2100 TEM. The TEM and connecting beamline with a suite of pumps, beam profile monitors, Faraday cups, valves, slits, viewing screens, bending magnets, focusing magnets, and steering magnets can be seen in Figure 1A. All of these components permit the delivery of a variety of ion beams ranging from 2.5 MeV protons to 3 MeV Au ions with current ranging from 1 pA to 100 nA. In Figure 1B, A beam burn produced by 14 MeV Si into the sample region of a TEM single tilt holder tilted 30º can be seen. This final alignment ensures that the entire sample region is exposed to the ion beam during the *in situ* ion irradiation TEM experiments. Here details of one of the initial in-situ ion irradiation experiments are presented. A TEM foil of HT9 received from Los Alamos National Laboratory, and prepared by focused ion beam (FIB) lift-out, was irradiated with approximately 10 nA current using a 3 MeV Cu^{3+} ion beam in time intervals ranging from 5 mins to 1 hr for a total irradiation time of 6 hrs. In addition to the *in situ* ion irradiation capabilities, this TEMhas been outfitted with a beta version of the Protochips gas cell system that permits the flow of a variety

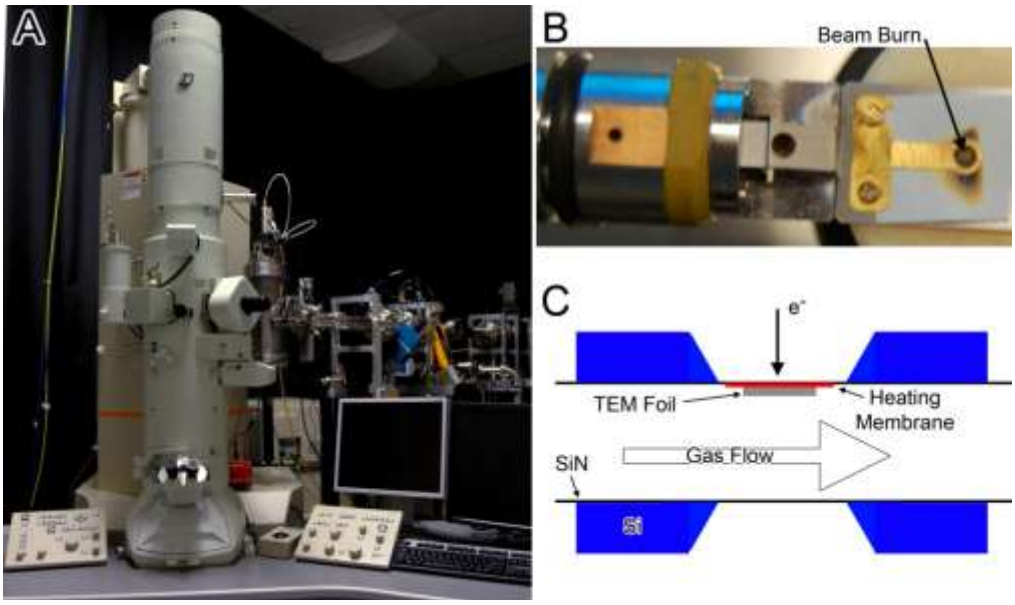

Figure 1. A) Image of I^{3}TEM at Sandia National Labs B) Photograph of a beam burn spot on a single tilt TEM stage created by 14 MeV Si beam. C) Schematic of the gas cell TEM stage.

of gases over a resistively heated, conductive ceramic membrane that can be heated up to 1200 ºC. In the first experiment performed using this stage at Sandia National Laboratories, a Zircaloy TEM foil prepared by FIB lift-out was placed on the heating membrane on the top chip of the gas cell stage (see Figure 1c). The image quality of such a technique was investigated by comparing images taken of the Zircaloy sample through a single 5 nm thick SiN window in vacuum and then through two 5 nm thick windows and a 5 μm gap filled with nominally one atmosphere of room air. The sample exposed to air was then annealed at various temperatures ranging from nominally 300 ºC to 1200 ºC for time intervals between 15 minutes and one hour.

RESULTS AND DISCUSSION

The *in situ* ion irradiation TEM developed at Sandia has been applied to a variety of materials systems and here we present the initial results from the ion irradiation of an HT9 sample exposed to 3 MeV Cu^{3+} ion beam at approximately 10 nA. The initial results of these experiments can be seen in Figure 2. In Figure 2A, the initial microstructure of the FIB produced HT9 sample shows elongated grains with extensive deformation defect structures and limited to no signs of FIB induced damage. The sample was exposed to the 3 MeV Cu^{3+} ion beam for two hours (Figure 2B), three hours (Figure 2C), and six hours (Figure 2D) showing signs of microstructural evolution resulting from the ion beam exposure.

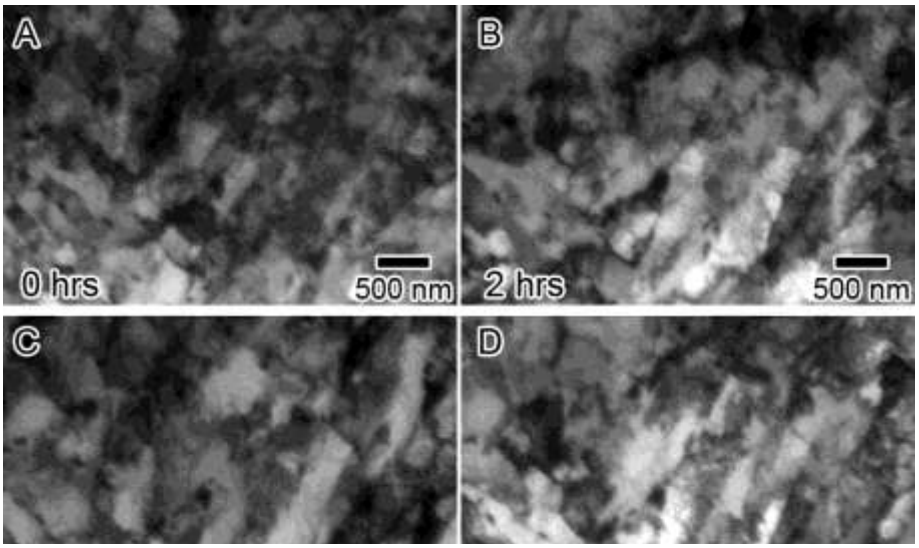

Figure 2. Ion irradiation damage in HT9 steel from 3 MeV Cu^{3+} A) Initial microstructure, B) Microstructure after 2 hours, C) after 3 hours, and D) after 6 hours of exposure.

Despite the extent of ion-irradiation received by the HT9 TEM foil, perceivable radiation-damage-induced morphological changes could not be observed. This lack of microstructural evolution is hypothesized to be a result of non-optimized experimental conditions, which will be addressed in future experiments. Furthermore, the FIB sample preparation resulted in a cantilever structure with the TEM sample located at the end of the structure. This design resulted in significant vibration of the sample during the ion beam exposure due to the resulting thermal fluctuations. Thus, improvements in sample preparation and optimization of experimental conditions are required to obtain ideal imaging conditions for the expected radiation damage and then maintain the image condition during the ion beam irradiation [3].

Figure 3a shows an overview of the bottom window and top window with heating membrane in the gas cell stage. The bottom window was intentionally cracked to allow vacuum to be pumped within the gas cell. On the top window, uniformly spaced holes that are approximately 8 µm in diameter are seen within the conductive ceramic heating membrane. (Figure 3b). Zircaloy foil obtained by FIB milling was placed on one of these holes. The foil is approximately 11 µm long and 5 µm wide (Figure 3c)with an electron transparent region less than 100 nm thick. Further examination at higher magnification of the electron transparent region of the foil reveals several distinct grains and a large grain approximately 4 μm^2 in area. A region with dark contrast, most likely a secondary phase precipitate less than 0.06μm^2 in area, is also visible (Figure 3d). Within the foil, randomly spaced dark spots are present. These spots are hypothesized to be contamination resulting from incomplete removal of the photoresist coating used during production of the gas cell chamber. Finally, the dark circular features outside the dashed arc (Figure 3d) represent the morphology of the underlying resistive heating membrane.

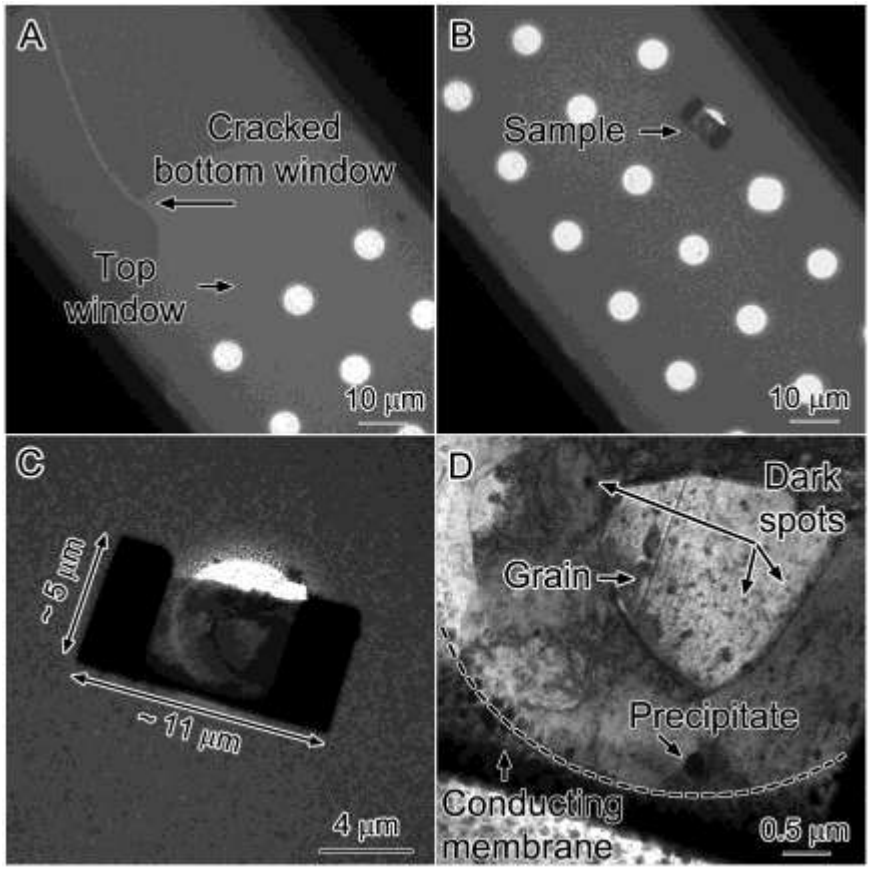

Figure 3. A) Overview of the gas cell that shows a cracked bottom window, B) Overview with a Zircaloy lamella, C) Dimensions off the Zircaloy lamella placed on the heating membrane, D) Detailed morphology of the lamella.

Examination of the same foil with intact top and bottom windows and the introduction of room air at ambient temperature (Figure 4a) shows deterioration of resolution due to expected additional scattering of electrons by the 500 nm of air, after initial scattering by the foil. Despite this loss in resolution, prominent features of the foil that were observed under vacuum are still visible. The gas cell was then rapidly brought to 300° C and significant change was observed over the 15 minutes of annealing. The evolution observed was not associated with changes in the Zircaloy, as negligible change in the Zircaloy morphology occurred (Figure 4b). It is thought that the change in image character was a result of pre-existing contamination on the gas-cell windows vaporizing and thereby substantially improving image quality. Following the 15

minute anneal at 300° C, the temperature of the gas cell was raised to 600° C and a dramatic morphology change within the sample was observed almost instantaneously.

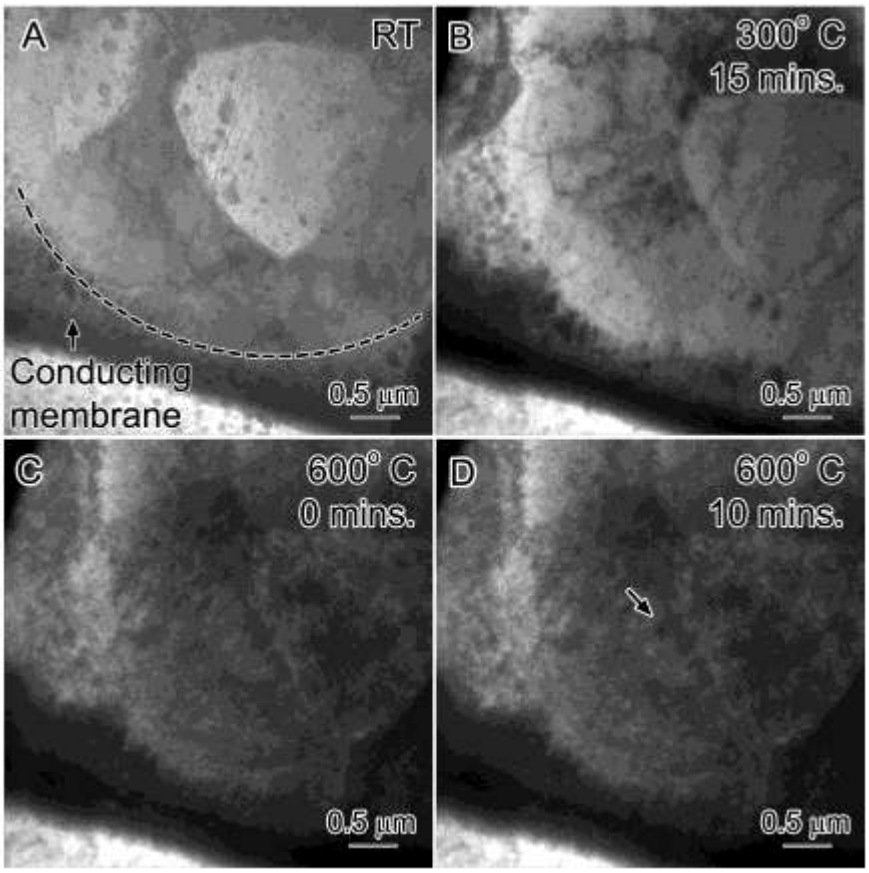

Figure 4. Images of Zircaloy lamella at nominally atmospheric pressure A) initial structure. B) 15 min at 300 ºC, C) 600 ºC, and D) 600 ºC after 10 minutes.

These results may be understood by considering that past studies have shown zirconium to have chemical affinity to oxygen that most likely results in a thin oxide film formation occurring immediately after exposure to ambient conditions [4, 5]. Furthermore, studies predict that the subsequent oxide film growth is temperature dependent, and exhibits parabolic, sub-parabolic, cubic or linear time dependence in different environments [6-8]. Although the mechanisms for oxide growth kinetics under various conditions is still actively debated, the dramatic morphological changes associated with the observed oxidation observed in the Zircaloy foil with relatively thin initial thickness (< 100 nm), may be conservatively modeled as a slab of Zircaloy exposed to a continuous flow of air according to the relationship $\xi^2 = Kt$ [9], where ξ is the oxide thickness, K a temperature dependent parameter ~ 9.47×10^{-13} m^2/hr at 600° C, and t is the time for oxidation. Thus, calculations predict that annealing at 600° C for 10s leads to an oxide growth of approximately 50 nm, which is approximately half the foil thickness. In the present context, it is highly likely that most of the Zircaloy foil oxidizes during the rapid temperature ramp from 300° C to 600° C and subsequent temperature stabilization at 600° C. Although negligible morphology changes are observed after 10 minutes of annealing, subtle localized morphological changes, such as those arrowed in Figure 4d do manifest. Further annealing at 600° C does not change the morphology, nor do higher temperature anneals at 800° C for 15 minutes, 1000° C for 15 minutes, and 1200° C for one hour result in any further change in morphology.

CONCLUSIONS AND FUTURE WORK

The initial *in situ* ion irradiation TEM experiments performed at Sandia National Laboratories that are seen in Figures 1B and 2 demonstrate that these capabilities have been

achieved and applied to a TEM foil of HT9. The experiences learned from these initial experiments are being applied to a variety of systems exposed to radiation environments, ranging from high-z scintillating nanoparticles to cladding materials. In addition to the application of the *in situ* ion irradiation TEM to various systems, work is under way to develop a concurrent ion irradiation capability that will permit simultaneous exposure of heavy ion irradiation from the 6 MV Tandem accelerator with light gas ions from a 10 kV Colutron. The continued improvement of this facility is expected to expand the materials systems that the *in situ* ion irradiation TEM at the Ion Beam Laboratory can study, providing new fundamental understanding of the materials response to both displacement damage and implanted gas molecules.

The preliminary gas cell results indicate that the technique is viable for studies of oxidation, corrosion, and second-phase formation *in situ* in the TEM. In summary, although the oxidation of Zircaloy is predicted and expected during high temperature annealing at nominally atmospheric conditions, gas cell *in situ* heating TEM offers a unique and powerful way to study morphology evolution of nuclear cladding materials as a function of temperature and environment. These results also demonstrate the importance of careful sample preparation and thorough cleaning of the gas cell chips prior to each experiment; improvements in these areas will be an immediate focus to assure that potential pitfalls related to gas cell pressure, imaging area, and contamination are avoided.

A gas manifold system for flow of hydrogen and other gases is currently being constructed to enable experiments on hydrogen embrittlement and hydride formation in cladding materials. The formation of hydrides, their dissolution, and reprecipitation, is particularly important for long term dry storage of currently-used fuel assemblies, as the size, shape, and orientation of hydrides is known to play a strong role in the mechanical properties of spent claddings.

ACKNOLEDGEMENT

The authors would like to thank Drs. D. Enos, R.F. Weiner, S.A. Maloy, and B.L. Doyle, as well as G.L. Bryant, D.L. Buller, and M.J. Rye for the various advice and assistance provided to this project. Sandia is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly-owned Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

REFERENCES

[1] E.P. Butler, in: Electron Microscopy and Analysis, 1979, 3-6 Sept. 1979, Inst. Phys, Brighton, UK, 1980, pp. 307-312 BN - 300 85498 85143 85498.
[2] J.A. Hinks, Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms, 267 (2009) 3652-3662.
[3] M.L. Jenkins, Journal of Nuclear Materials, 216 (1994) 124-156.
[4] A. Grandjean, Y. Serruys, Journal of Nuclear Materials, 273 (1999) 111-115.
[5] R.A. Perkins, Journal of Nuclear Materials, 68 (1977) 148-160.
[6] T. Arima, K. Moriyama, N. Gaja, H. Furuya, K. Idemitsu, Y. Inagaki, Journal of Nuclear Materials, 257 (1998) 67-77.
[7] E. Hillner, D.G. Franklin, J.D. Smee, Journal of Nuclear Materials, 278 (2000) 334-345.
[8] M. Steinbrueck, M. Boettcher, Journal of Nuclear Materials, 414 (2011) 276-285.
[9] H.I. Yoo, B.J. Koo, J.O. Hong, I.S. Hwang, Y.H. Jeong, Journal of Nuclear Materials, 299 (2001) 235-241.