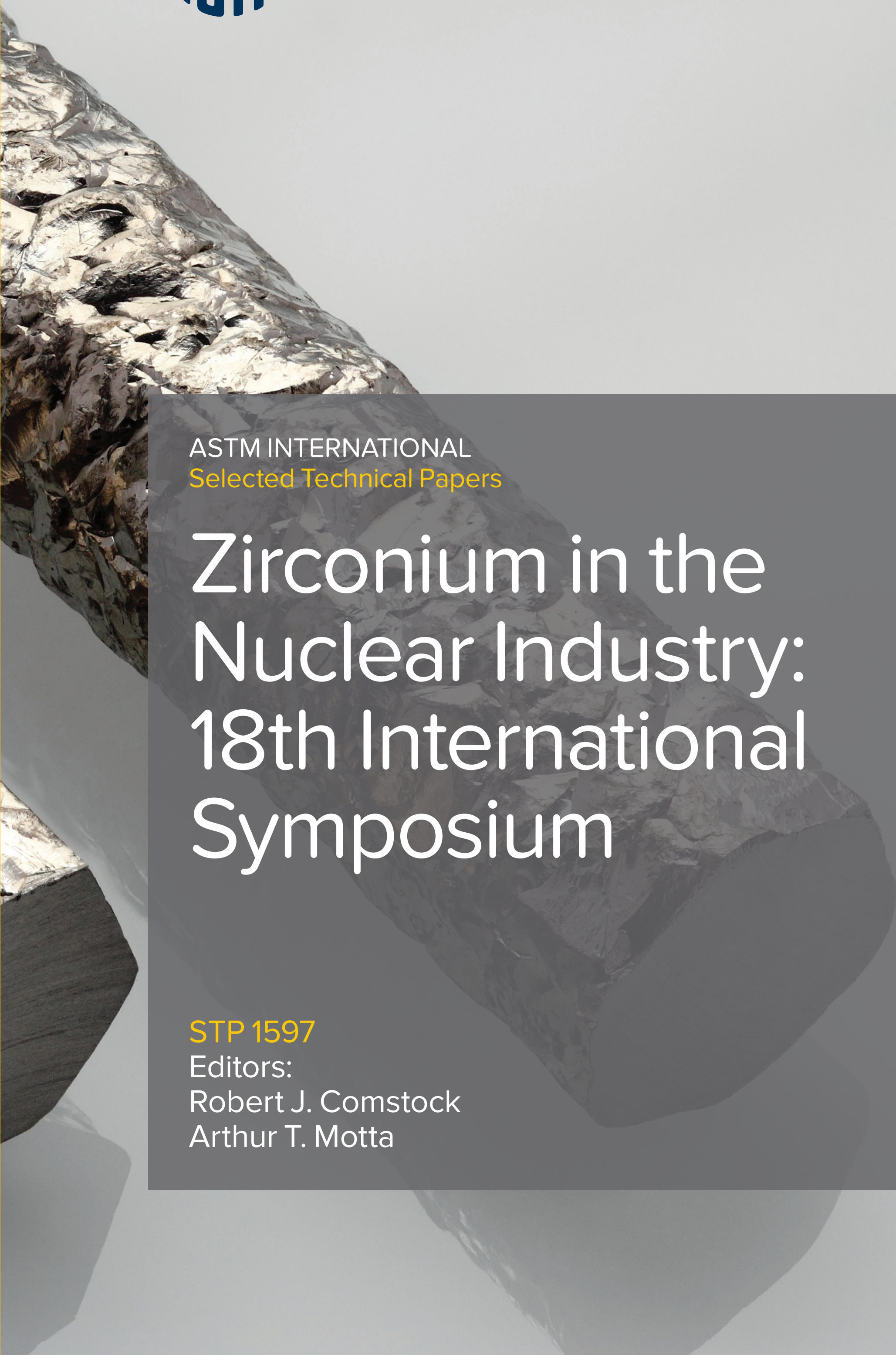

ASTM INTERNATIONAL
Selected Technical Papers

Zirconium in the Nuclear Industry: 18th International Symposium

STP 1597

Editors:
Robert J. Comstock
Arthur T. Motta

SELECTED TECHNICAL PAPERS
STP1597

Editors: Robert J. Comstock and Arthur T. Motta

Zirconium in the Nuclear Industry: 18th International Symposium

ASTM STOCK #STP1597
DOI: 10.1520/STP1597-EB

ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959
Printed in the U.S.A.

Library of Congress Cataloging-in-Publication Data

ISBN: 978-0-8031-7641-6

ISSN: 1050-7558

Peer Review Policy

Each paper published in this volume was evaluated by two peer reviewers and at least one editor. The authors addressed all of the reviewers' comments to the satisfaction of both the technical editor(s) and the ASTM International Committee on Publications.

The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of the peer reviewers. In keeping with long-standing publication practices, ASTM International maintains the anonymity of the peer reviewers. The ASTM International Committee on Publications acknowledges with appreciation their dedication and contribution of time and effort on behalf of ASTM International.

Citation of Papers

When citing papers from this publication, the appropriate citation includes the paper authors, "paper title," STP title, STP number, book editor(s), ASTM International, West Conshohocken, PA, year, page range, paper doi, listed in the footnote of the paper. A citation is provided on page one of each paper.

Printed in Eagan, MN
January, 2018

Foreword

THIS COMPILATION OF Selected Technical Papers, STP1597, *Zirconium in the Nuclear Industry: 18th International Symposium*, contains peer-reviewed papers that were presented at a symposium held May 15–19, 2016, in Hilton Head, South Carolina, USA. The symposium was sponsored by ASTM International Committee B10 on Reactive and Refractory Metals and Alloys and Subcommittee B10.02 on Zirconium and Hafnium.

Symposium Chairpersons and STP Editors:

Robert J. Comstock
Westinghouse Electric Co., LLC (retired)
Pittsburgh, PA

Arthur T. Motta
Penn State University
University Park, PA

Contents

Mechanisms of Corrosion and Hydrogen Pickup

Irradiation Effects on Corrosion

Irradiation Damage, Creep, and Growth

In-Reactor Performance

Hydrogen Effects and Dry Storage

Overview

This Selected Technical Papers (STP) publication contains papers presented at the *18th International Symposium on Zirconium in the Nuclear Industry*, which was held in Hilton Head, South Carolina, from May 15 to 19, 2016. This symposium has long been the traditional meeting place for researchers who work in zirconium technology as applied to the nuclear industry.

The 2016 symposium had 137 participants from 13 countries with representation from the Americas, Europe, and Asia. The symposium featured 42 platform presentations as well as a poster session with 24 contributions. This STP includes 43 peer-reviewed papers, among which are the papers from the winners of the William J. Kroll Zirconium Medal for 2013, 2014, and 2015. We are happy to note the increased participation of young researchers and students, many of whom presented their work, either as oral presentations or posters. A total of 20 students attended the conference, a most welcome development for the formation of the new generation of researchers in the field.

For almost 50 years, this symposium has been the place where archival research in zirconium technology is published, with researchers often saving their most noteworthy work for this conference. The first symposium of this series was held in Philadelphia in 1968 with subsequent symposia held every two to three years in places around the world. The proceedings of each symposium in the series constitute significant contributions to the understanding and development of zirconium alloys for application in nuclear power reactors and have been documented consistently in STP publications, collections of which grace our bookshelves. This symposium is distinctive in that the attendees hear every presentation, which often is followed by stimulating discussions that are prompted by questions from the audience. As in past symposia, these questions are included at the end of each paper in this volume, along with written responses by the authors. This unique and valuable feature of this publication series allows the attendees to provide different perspectives on the work while also providing the authors a chance to further clarify their papers.

Much of the understanding that was empirically obtained over the years about the behavior of zirconium alloys is now being studied in greater depth to derive mechanistic understanding. This is enabled by new characterization techniques, including synchrotron radiation techniques, atom probe, neutron radiography, advanced techniques in electron microscopy, and detailed electrochemical methods. These techniques provide new perspectives on studying these materials, which may allow us to address basic questions, such as identifying the specific role of alloying elements in corrosion, hydrogen pickup, and irradiation growth. Especially when coupled with enhanced computing power and new materials simulation methods, the potential exists for significant advances in understanding to be achieved.

We divided the papers included in this STP into the following categories:

Processing and Mechanical Properties
Mechanisms of Corrosion and Hydrogen Pickup
Irradiation Effects on Corrosion
Irradiation Damage, Creep, and Growth
In-Reactor Performance
High-Temperature Transients
Hydrogen Effects and Dry Storage

These broad categories encompass the range of challenges that are relevant to the nuclear community and currently are being addressed in research conducted in industry, national laboratories, and universities.

Waterside corrosion of cladding continues to remain an area of active research. Recent research, however, has focused more on addressing operational concerns and understanding mechanisms of corrosion rather than on introducing new alloys with improved corrosion performance. One exception to this is the nascent effort to develop accident tolerant fuel cladding, which is discussed in the following.

The desire of the nuclear industry to increase the amount of dissolved hydrogen in pressurized water reactor (PWR) coolant to reduce primary water stress corrosion cracking of nickel-based alloys prompted an industry study (Wells et al.) to assess the potential impact of this change on the hydrogen pickup of the cladding. The observed increase in the hydrogen pickup fraction (HPUF) in Zircaloy-2 at high burnup in boiling water reactors (BWRs) led to detailed studies of the oxidation state of alloying elements in the oxide formed on irradiated Zircaloy-2 by microbeam XANES (x-ray absorption near-edge spectroscopy). Shivprasad et al. established a link between the presence of metallic nickel in the oxide layer and increased HPUF in Zircaloy-2.

Many papers focus on the influence of irradiation on corrosion, whether through changes to the metal, to the oxide layer, or to the corroding solution by gamma radiation (Rishel and Kammenzind). Detailed microstructural evaluations that provide the knowledge base to enable modeling of the coupling between oxidation and hydrogen pickup were performed by Couet et al. They identified the impact of alloying additions on the oxide resistivity and showed that lower electronic resistivity of the oxide layers formed in Zr-Nb alloys was consistent with the reduced hydrogen pickup. Long-term corrosion results of Zircaloy-4 coupons in the Advanced Test Reactor demonstrated the significant corrosion enhancement of Zircaloy-4 resulting from irradiation (Kammenzind et al.). They identified changes in the metal microstructure as the dominant contribution to the observed increase in corrosion. Markelov et al. examined the impact of irradiation on the metal microstructure of Zr-Nb and Zr-Nb-Sn-Fe alloys and concluded that the corrosion of Zr-Nb improved during irradiation because of the formation of niobium-rich radiation-induced precipitates. Although these results on Zircaloy-4 and Zr-Nb are consistent with previous studies, the basic mechanism relating metal microstructure to corrosion performance still eludes researchers.

Detailed characterization of the evolving microstructure at the oxide-metal interface and in the growing oxide was presented in several papers and included not only autoclaved samples but also irradiated specimens. Jublot et al. reported on the oxide formed in autoclaves on Zircaloy-4 with and without a hydride rim. Utilizing automated crystal orientation mapping, they concluded that the higher oxidation of the hydride rim was consistent with both the increased oxide grain boundary density and larger misorientation between oxide grains. Two papers presented results utilizing ion irradiation as a surrogate for neutrons. Radiation damage of the oxide formed on Zircaloy-4 (Colas et al.) resulted in an increase in oxidation kinetics, whereas damage of the oxide formed on M5 decreased kinetics (Tupin et al.). Although it is interesting that the effects are parallel to the previously mentioned in-reactor results for Zircaloy-4 and Zr-1Nb, it remains to be confirmed that the oxide defects from ion irradiation are also present in neutron-irradiated samples.

For the first time, characterization of oxides formed on E110 and E635 in VVER-1000 reactors was presented (Shevyakov et al.). They conclude that the density of micropores in the oxide formed on E110 remains low, consistent with protective behavior. In contrast, high-microporosity density was reported for E635 and was attributed to the diffusion of iron and niobium from Laves phase particles. Because the microporosity in autoclaved E635 samples was comparable, they concluded that the corrosion acceleration during in-reactor operation was not the result of microporosity of the oxide film. Garner et al. provided a different perspective, showing extensive intergranular porosity in oxide formed on three-cycle Zircaloy-2 and followed by networks of interconnected cracks and porosity in six-cycle Zircaloy-2 that were not present in nonirradiated autoclaved samples. Hu et al. performed extensive characterization of oxide films formed on both autoclaved Zr-1Nb as well as Zr-1Nb irradiated for one 18-month cycle in a PWR. Among their findings was a strong correlation between oxide porosity and oxidation rate, with α-annealed Zr-1Nb in both autoclave and in-reactor environments having a significantly lower corrosion rate and porosity than an α+β-annealed Zr-1Nb autoclaved in water. These papers highlight the challenge in interpreting results and achieving a unified understanding of the corrosion mechanism, as research often is limited by the availability of in-reactor samples, and the examination of which provides but a snapshot of a process that evolves continuously during in-reactor operation.

Dimensional stability of zirconium alloy components through creep and growth during service continues to challenge researchers. Two papers presented results on Zr-Nb-Sn-Fe alloys designed to provide reduced dimensional changes through end of life. Doriot et al. provided results from irradiation of Q12 (Zr-1Nb-0.5Sn-0.1Fe), which was developed for structural components, and Cantonwine et al. discussed the development of NSF (Zr-1Nb-1Sn-0.4Fe) for application in BWRs for reduced channel bow. Microstructural evaluations of irradiated Q12 and other Zr-Nb-Sn-Fe alloys by Doriot et al. show that despite early rejection of iron from the Laves phase into the matrix, increased iron in the presence of niobium and tin decreases <c>component linear loop density and likely delays the onset of breakaway growth. The results of Doriot et al. are consistent with the results from an extensive irradiation growth program reported by Yagnik et al., in which 36 Zr-Sn-Nb alloy variants with iron ranging from 0.01 wt.% to 0.4 wt.% were irradiated in BOR-60. Their results show that niobium reduces growth and that the addition of iron results in a significant growth reduction in Zr-Sn, Zr-Nb, and Zr-Nb-Sn alloys. In addition, Yagnik et al. showed that hydrogen in excess of the solubility limit (>100 wt. ppm) results in a significant increase in the growth rate and earlier onset of accelerated growth than non-hydrogen-charged samples. In addition, Topping et al. examined the microstructural development of Zr-0.1Fe and Zircaloy-2 following proton irradiation. They correlated iron redistribution and formation of iron nanoclusters in Zircaloy-2 to the delay in c-loop formation, providing a possible explanation for the decreased growth because of the iron reported by Doriot et al. and Yagnik et al. Finally, papers on the temperature and flux dependence of creep (DeAbreu et al.) and on the effect of hydrogen on creep and growth (Foster et al.) were presented.

A research area of continued interest is the high-temperature behavior of cladding motivated by proposed U.S. Nuclear Regulatory Commission rulemaking regarding loss of coolant accidents (LOCA). Two papers examined the detrimental impact of air on the oxidation of cladding at high temperature (1100 K to 1500 K), by Haurais et al., and in the spent fuel pool, by Kasperski et al. Grosse et al. demonstrated the in situ measurement of hydrogen uptake by neutron radiography during high-temperature steam oxidation of cladding. The technique clearly showed the rapid ingress of hydrogen associated with breakaway oxidation. Malgin et al. explored the impact in chemistry in Zr-Nb and Zr-Nb-Sn-Fe alloys on ductility following high-temperature (1273 K to 1473 K) steam oxidation, while Mueller et al. showed the impact of hydrogen on the post-quench ductility of Zircaloy-4, ZIRLO®, and Optimized ZIRLO™ cladding. The work by Hózer et al. shows that secondary hydriding of E110 is similar to that observed in other alloys. Nguyen et al. studied the influence of heating rate on flow stress of zirconium alloy cladding during a high-temperature transient, finding that the α-to-β transformation is delayed upon fast heating rate, which causes a lower flow stress. Turque et al. studied in detail the mechanical behavior of zirconium alloys during high-temperature transients, especially the influence of hydrogen and oxygen on ductility and flow stress. The results from these latter two studies will be useful for the improvement of models during transients.

One paper on accident-tolerant fuel in the proceedings (Van Nieuwenhove et al.) presents the results of a study on the behavior of CrN, TiAlN, and AlCrN coatings on Zircaloy-4, with CrN showing the best behavior following irradiation in the Halden reactor under PWR conditions. Comparison of these results with previously successful use of TiAIN coatings indicates that the layer architecture, bond layer, and deposition method have a strong influence on the layer stability at high temperature.

Concerning radiation damage, much work is now being done with charged particle irradiations that can deliver much higher dose rates than neutron irradiation. Additionally, the quantification of radiation damage using synchrotron radiation diffraction is a promising new area of study. This was presented by Balogh et al., in which they relate the x-ray diffraction signal to dislocation densities measured by transmission electron microscopy. Walters et al. presented calculations on equivalent damage between reactors, which has been an issue of persistent interest.

In the area of mechanical properties and hydride embrittlement of cladding, increasingly detailed modeling and theoretical understanding coupled with targeted experiments are helping to develop basic understanding of deformation mechanisms and failure processes of hydrided cladding in dry storage. One of these studies was presented by Kesterson et al. The issue of hydride reorientation during preparation for dry storage continues to be important, and more detailed studies (Cinbiz et al.) have shown that the biaxiality of the stress state is important to determine the critical stress for hydride reorientation during cooling under stress. Atomistic modeling as well as polycrystalline modeling at the mesoscopic level have yielded new insights on deformation strain path and damage accumulation (Onimus et al.). In particular, the work by Christensen et al. presents new efforts on multiscale materials modeling, especially as applied to growth. Although the fabrication area, in the words of one of the session chairs, may now be considered a mature area, two interesting papers were presented by Gaillac and Barberis on the computational modeling of hot extrusion during fabrication and by Daniel et al. on texture development in Zr-Nb alloys using x-ray diffraction.

During this symposium, the William J. Kroll Zirconium Medals for the years 2013–2015 were presented. The joint recipients for 2013 were Dr. Allan Rogerson and Dr. Robert Murgatroyd, who were recognized for their research on the long-term irradiation growth behavior of zirconium alloys. The 2014 Kroll Medal was presented to Professor Arthur T. Motta for contributions in zirconium metallurgy in the areas of oxidation, hydriding, deformation, and radiation damage, and the 2015 Kroll Medal was presented to Dr. Toyoshi Fuketa for research related to the behavior of zirconium alloy fuel cladding during reactivity-initiated accidents and LOCAs. At the awards ceremony, Dr. Rogerson, Prof. Motta, and Dr. Fuketa presented reviews of their work that provided the basis for their awards. They also contributed Kroll Award papers that are included in this volume.

For the first time in the symposium, a Best Poster Award was selected from among the contributions in the poster session by a group of judges encompassing various areas of expertise. A total of 24 posters were presented at the conference. The winning poster selected by the committee was entitled "Stopping Delayed Hydride Cracking in Zirconium Alloys by Heating" and was authored by Sean Hanlon, Christopher Coleman, Andrew Buyers, and Glenn McRae. The award was presented to the authors at the end of the symposium.

Following the symposium, a committee of technical experts covering a breadth of experience in the zirconium nuclear industry selected the winner of the John H. Schemel Best Paper Award based on technical excellence, relevance to the nuclear industry, and groundbreaking research. The winner of the award was the paper entitled "Understanding Corrosion and Hydrogen Pickup of zirconium Nuclear Fuel Cladding Alloys: The Role of Oxide Microstructure, Porosity, Suboxide and SPPs" by Jing Hu, Brian Setiadinata, Thomas Aarholt, Alistair Garner, Arantxa Vilalta-Clemente, Jonna Partezana, Philipp Frankel, Paul Bagot, Sergio Lozano-Perez, Angus Wilkinson, Michael Preuss, Michael Moody, and Chris Grovenor. We offer our sincere congratulations to the winners. The award will be given at the next symposium to be held in Manchester, England, in 2019.

In looking through the overviews written by previous editorial chairs, many of the important issues that are now of concern to the industry had been identified and were being studied in the prior symposia. This indicates that knowledge has been accruing in many of the session topics of interest to the community. We are happy that this STP publication can contribute in some part to this continuous process of scientific discovery, mechanistic understanding, and technology development to further improve the performance of nuclear fuel worldwide.

Arthur T. Motta
Robert J. Comstock

ASTM INTERNATIONAL
Helping our world work better

ISBN: 978-0-8031-7641-6
Stock #: STP1597

www.astm.org