

Zirconium *in the* Nuclear Industry

TENTH INTERNATIONAL SYMPOSIUM



Anand M. Garde
E. Ross Bradley

EDITORS

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Zirconium in the Nuclear Industry: Tenth International Symposium

Anand M. Garde and E. Ross Bradley, Editors

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

The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editors, but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution to time and effort on behalf of ASTM.

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December 1994

Foreword

The Tenth International Symposium on Zirconium in the Nuclear Industry was held in Baltimore, MD on 21–24 June 1993. The sponsor of the event was ASTM Committee B-10 on Reactive and Refractory Metals and Alloys in cooperation with the Minerals, Metals and Materials Society.

The Symposium Chairman was A. M. Garde, ABB Combustion Engineering Nuclear Operations, and the Editorial Chairman was E. R. Bradley, Sandvik Special Metals. Serving as Editors of this publication were A. M. Garde and E. R. Bradley.

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Overview

This volume contains papers presented at the Tenth International ASTM Symposium on Zirconium in the Nuclear Industry, held in Baltimore, MD in June of 1993. The symposium was attended by 200 zirconium experts from 16 countries. The symposium consisted of seven platform sessions and a poster session. The platform session titles, and cochairmen for each session were as follows:

- Hydrogen Effects—D. G. Franklin and F. Garzarolli
- Pressure Tubes—B. A. Cheadle and D. Pickman
- Fabrication—E. Tenckhoff and J. B. Narayan
- Lithium Effects and Second-Phase Particles—G. P. Sabol and C. Lemaignan
- Mechanical Properties—R. B. Adamson and G. D. Moan
- Oxide Characterization—B. Cox and C. M. Eucken
- In-reactor Corrosion—L. van Swam and P. Rudling

Without the thorough technical review of each manuscript performed by the 34 reviewers, publication of these proceedings would have been impossible. The best paper presented at the platform session of the symposium was selected for the John Schemel award on the basis of technical merit, originality, and general presentation. The paper selected for the John Schemel award for the Tenth Zirconium Symposium is entitled "Oxidation of Intermetallic Precipitates in Zircaloy-4: Impact of Irradiation," by D. Pêcheur, F. Lefebvre, A. T. Motta, C. Lemaignan and D. Charquet. The award will be presented at the Eleventh Zirconium Symposium, Sept. 1995, in Germany.

This volume also contains papers written by the recipients of two Kroll awards presented at the Symposium. The Kroll papers are "Development of Zirconium-Barrier Fuel Cladding," by J. S. Armijo, L. F. Coffin, and H. S. Rosenbaum and "Zirconium Alloy Performance in Light Water Reactors: A Review of UK and Scandinavian Experience," by D. O. Pickman. The editors acknowledge the cooperation of the Kroll Award Committee Chairman, G. P. Sabol, in facilitating publication of the Kroll papers. Twenty papers were presented as posters in the poster session. The titles and authors of the poster presentations are listed in the Appendix following this section.

The recent trends in the nuclear industry towards higher fuel discharge burnups for better fuel use and higher heat ratings and coolant temperatures for better thermal efficiency have significantly increased the technical interest on corrosion of zirconium alloys. Accordingly, papers relating to corrosion had a dominant position at the symposium. It is clear that the corrosion resistance of the current zircaloys will not be adequate for these more aggressive service conditions. Consequently, considerable effort has been devoted to evaluating the effects of processing history and alloying elements on the corrosion resistance of zircaloys and also to new alloys outside the composition range of conventional materials for nuclear reactor applications.

Four separate sessions were devoted to various aspects of zirconium alloy corrosion: Hydrogen Effects, Lithium Effects and Second-Phase Particles, Oxide Characterization, and In-Reactor Corrosion. The remaining symposium sessions were: Pressure Tubes, Fabrication, and

Mechanical Properties. The papers in this volume are organized by the topical sessions in which they were presented.

The technical information contained in this book is valuable to zirconium alloy producers, nuclear fuel fabricators, reactor materials designers and development engineers, utility plant operators, and regulators. The data are useful in achieving safe, economic, and efficient power generation from the nuclear energy.

Hydrogen Effects

Hydrogen pickup and its effect on the mechanical and corrosion behavior of the zirconium alloy components used in the nuclear industry is becoming an important issue. The low hydrogen uptake of Zr-2.5Nb is associated with the β -Zr phase that contains 20% Nb. This observation supports the relationship between the electronic conductivity of the oxide and hydrogen pickup by the underlying metal. The delayed hydrogen cracking velocity of Zr-2.5Nb cold-worked material increases due to irradiation and K_{ID} is reduced by radiation hardening. For Zircaloy, the hydriding rate is proportional to the corrosion rate and hydrogen absorption depends on the final heat treatment, integrated annealing parameter, tin level, Ni level, Cr Level, and Fe/Cr ratio. The hydrogen pickup fraction is not constant and appears to be inversely proportional to the extent of corrosion. A scanning electron microscopic technique (SEM) applicable to both irradiated and unirradiated zirconium alloys was described to study the distribution and morphology of hydrides in zirconium alloys. It was proposed that hydroxyl groups are probably picked up by the oxide layer, mainly at the grain boundaries of the outer porous layer, and that protons are the species permeating the dense barrier oxide layer to charge hydrogen in the underlying metal layer.

Pressure Tubes

Eighty-seven of the world's reactors that either have been built or are under construction use pressure tubes rather than pressure vessels to contain the hot pressurized coolant. Zircaloy-2 was used for the pressure tubes in the early reactors. Currently, Zr-2.5Nb, an alloy that is stronger than Zircaloy-2, is used for the pressure tubes. The metallurgical condition of the Zr-2.5Nb tubes varies in different countries: cold worked and annealed (Russia); cold worked and stress relieved (Canada); and water quenched, cold worked, and aged (India and Japan).

The main concern for pressure tubes is their service life. The hot pressurized water and neutron flux produce an environment of stress, temperature, corrosion, and lattice damage. These result in changes in dimensions (creep and growth); changes in mechanical properties (increases in strength and DHC velocity, decreases in ductility and fracture toughness); and changes in chemical composition (hydrogen ingress).

The papers in this book that are associated with the pressure tube materials addressed all of these concerns. In CANDU pressure tubes, there is an initial decrease in fracture toughness with fluence and then little further change; this correlates well with the dislocation density. There is also a direct relationship between unirradiated and irradiated fracture toughness. Hence, from tests on new pressure tubes, their behavior during service can be predicted. In addition, it has been found that chlorine, which is an impurity element, reduces the fracture toughness if there is more than 1 ppm present in the material. The Fugen heat-treated pressure tubes had similar increases in strength and reductions in ductility and fracture toughness with fluence as the CANDU tubes. This is surprising as their microstructures are very different. However, the magnitude of the changes may be different and since different fracture toughness specimens were used, the results are difficult to compare directly. The irradiation growth behavior of small specimens from CANDU pressure tubes is quite variable. A key parameter

has been found to be the iron concentration; increasing iron from 500 to 2000 ppm reduces the growth by about half. It is suggested that the volume expansion due to hydride precipitation can contribute to the irradiation growth strain. Biaxial creep behavior was reported for Zr-2.5Nb tubes up to fluences of $7 \cdot 10^{25} \text{ n} \cdot \text{m}^{-2}$, showing the effect of texture on diametral strain rates. Advances have been made in the modeling of in-reactor creep, and the latest model takes into account grain interaction effects and shows how the texture can be optimized for the best in-reactor deformation behavior.

The big advance in pressure tube technology in the last few years has been the work showing the importance of 'impurity' elements and texture on the properties of the tubes. Reducing chlorine, carbon, and phosphorous increases fracture toughness, and increasing the iron decreases growth. In addition, careful attention to fabrication can considerably reduce the hydrogen concentration and control the distribution of oxygen between the α and β phases.

Fabrication

Fabrication process optimization for zirconium alloy components is important for two reasons. Firstly, the in-reactor performance (specifically the in-reactor corrosion resistance) of zirconium alloys strongly depends on the manufacturing history. Secondly, with the objective of 'zero defect' in-reactor performance, there is a continuing drive to eliminate the low-frequency manufacturing defects that contribute to the in-reactor failures. Important fabrication parameters enhancing the uniform corrosion resistance of Zircaloy-4 include higher annealing temperature immediately after the hot rolling step, low (<30%) second phase particle density in finished tube microstructure for fine (<100 nm) particles, Fe/Cr ratio of ~ 1.9 , Si level of ~ 70 ppm, high integrating annealing parameter, and low β quenching rate. Lowering of the tin content and increase of stress relief annealing temperature are beneficial to improve the in-PWR corrosion resistance. The stress corrosion cracking resistance is improved by flush pickling of the cladding tube inside surface. Irradiation growth is controlled by limiting the carbon level below 200 ppm. The nodular corrosion resistance of Zircaloy-2 is enhanced by introduction of an additional quench step from the ($\alpha + \beta$) phase region followed by only two tube reduction steps with higher value of Q . The severity and frequency of surface defects occasionally observed in cold pilgered Zircaloy-4 tubes are correlated to a damage function based on stresses and strains generated in the material during the pilgering operation.

Welding of zirconium alloy tubes introduces changes in texture within the weld region and also residual tensile stresses. These factors decrease the burst ductility, burst strength of the material, and promote delayed hydrogen cracking. To mitigate these harmful effects of weld, the tube wall thickness at the weld location is increased by 25% and the welded tube is subjected to a stress-relief annealing treatment.

Lithium Effects and Second-Phase Particles

Lithium is added to the PWR coolant to decrease the possibility of crud deposition on the fuel rods, and thereby reducing the transfer of activated products to the rest of the plant. While higher levels of lithium in the primary coolant are expected to lead to lower radiation levels in the secondary circuit components, possible concerns exist regarding (a) higher fuel cladding corrosion rate with higher lithium levels and (b) stress corrosion cracking of steam generator tubing. There are also indications that boron added to the primary coolant to control the reactivity would negate the lithium effect of corrosion acceleration of zirconium alloys. Two papers dealing with the lithium effect on zirconium alloy corrosion are included in this section of the book. (A third paper related to the lithium effect is part of the in-reactor corrosion section of the book.) The corrosion model in one paper predicts up to 30% corrosion enhancement at

50 GWd/MTU burnup for Zircaloy-4 irradiated in a high-temperature PWR when the lithium concentration in the coolant is increased from 2.2 to 3.5 ppm. The model considers the lithium-boron coordinated chemistry with a pH of 7.2 and 7.4 for these lithium levels. In another paper, the acceleration of corrosion in lithiated water is correlated with undissociated LiOH forming OLi groups on the oxide surface. In the presence of boron, the OLi groups are removed and thereby the corrosion rate decreases. The effect of lithium on corrosion of Zr-2.5Nb appears to be stronger than that on corrosion of Zircaloy-4.

The second phase particles in zirconium alloys have a strong effect on their uniform and nodular corrosion resistance. The important parameters in this regard are the particle size, particle composition, particle crystallinity, inter-particle distance, and so forth. Dissolution of second-phase particles in Zircaloys during irradiation is proposed to accelerate uniform corrosion at high burnups while eliminating nodular corrosion. The size of the second-phase particles depends on the processing history of the alloy. A higher amount of deformation during the tube reduction of Zircaloy-2 produces higher radial textured tubing with superior nodular corrosion resistance. A small precipitate size and short inter-particle distance also leads to superior nodular corrosion resistance. Analysis of second-phase particles in a new promising Zr-Sn-Fe-Cr-Nb alloy indicates a significantly lower solubility for niobium in this alloy compared to the Zr-Nb binary alloy. The new alloy has superior corrosion resistance and significantly lower hydrogen uptake than Zircaloy-4, while its mechanical properties are comparable to those of Zircaloy-4.

Mechanical Properties

Mechanical properties of irradiated zirconium alloy components strongly influence their in-reactor performance. Some of the mechanical properties of interest are creep, fatigue, stress corrosion cracking, embrittlement, delayed hydrogen cracking, and so forth. These properties depend on the evolution of the material microstructure due to the neutron bombardment. The phases present in the microstructure also depend on the material chemical composition and the fabrication history. The irradiation growth of the component that is an indication of the microstructural stability also depends on the above mentioned factors. Two important areas of technical interest are the correlation of in-reactor behavior to the laboratory behavior and modeling of mechanical properties to satisfy design requirements and mitigate operational concerns. The papers included in this proceeding address some of the points listed above.

Investigations related to the fatigue behavior of Zircaloys and zirconium show that irradiation does not affect the low-cycle fatigue behavior but decreases fatigue life in the high-cycle regime. This decrease in the fatigue life is related to strain localization and saturates with the extent of radiation damage. Fatigue crack growth rate is insensitive to the radiation damage but increases in the presence of water. Moreover, the increase is greater at higher oxygen content of the water. Microstructural evaluation of irradiated zircaloy shows that the breakaway growth in recrystallized and β -quenched Zircaloy at high fluences is associated with the generation of basal plane *c*-component dislocations. The irradiation induced changes in the second-phase particles (crystalline to amorphous transformation, dissolution, new phase particle precipitation) are shown to be temperature dependent. An elegant technique to study the stress corrosion crack propagation is described. Results confirm that the pseudo-cleavage of zirconium alloys produced during iodine SCC occurs along the basal planes, and cracking starts in those grains with maximum tensile stress on the basal plane. In another paper, the mechanical and corrosion properties of a new promising alloy are investigated as a function of the alloy composition. Possible correlations between anisotropy parameters of the irradiated and unirradiated states of Zircaloy-2 materials with different fabrication history are also discussed.

Oxide Characterization

Several aspects of the oxide layer morphology affect the corrosion resistance of the substrate zirconium alloy. These features include the phases present and their crystallinity, different sublayers formed in the oxide layer (including the layer next to the metal oxide interface called the "barrier layer"), the grain structure and the grain boundary orientations in the different sublayers, stresses developed in different sublayers during oxidation, porosity in different sublayers, chemical concentration of coolant additives within the oxide pores (for example, lithium hideout), and incorporation of the second-phase particles present in the substrate metal into the oxide layer as the oxidation proceeds. Recent results associated with most of the phenomena listed above are presented in papers included in this publication.

New information presented at the symposium is summarized below. The initial reaction rate of clean zirconium surface with H₂O molecules appears to be about one thousand times slower than the reaction rate with oxygen molecules. The laser Raman microprobe results indicate that at the metal-oxide interface, up to 40% of the oxide may be in the tetragonal phase. However, transmission electron microscopy (TEM) of the metal-oxide interface does not show the tetragonal phase, possibly due to a phase transformation associated with the relaxation of compressive stress during the specimen preparation. The stresses generated in the oxide and the proportion of tetragonal oxide near the metal-oxide interface vary cyclically in step with the cycles of oxidation kinetics. The magnitude of stresses developed in the oxide films may be related to the corrosion resistance of the substrate alloy. The oxidation of the intermetallic precipitates (as they are incorporated in the oxide layer) appear to modify the local stresses due to the volume change associated with such oxidation. The oxidation process may leave behind part of the iron content of the precipitate as iron particles in the oxide. This evolution of iron may have a major impact on the long-term in-reactor corrosion of zirconium alloys.

Morphological studies of oxide films continue to show that columnar ZrO₂ crystallites are associated with good oxidation resistance, and equiaxed microcrystallites are associated with nodular corrosion behavior and with more extensive cracking in post-transition uniform oxides. TEM results clearly show that the "barrier" layer at the metal-oxide interface is crystalline rather than amorphous. Interconnected porosity is observed at the crystallite boundaries in oxides formed in LiOH solutions accompanying the higher oxidation kinetics. The effects of the minor elements in the Zircalloys are only just becoming evident in terms of optimum Fe:Cr ratios in the intermetallics and the incorporation of Si in Zr₂(Fe/Ni) precipitates, that may provide a mechanism for the effect of Si on hydrogen uptake properties. If this incorporation of Si can modify the hydrogen absorption or recombination properties of the intermetallic, then it would probably also affect hydrogen uptake. In a similar manner, the precise stoichiometry of the Zr(Fe/Cr)_{2+x} phase may also have an impact on hydrogen absorption.

In-Reactor Corrosion

Corrosion resistance of zirconium alloys irradiated in both BWRs and PWRs to extended burnups is being investigated. The extended burnup data presented in this publication show new trends not apparent from the low-burnup data previously available. For optimum cladding corrosion resistance for BWR applications at both the low- and high-burnups, an intermediate range of second-phase particle size and beta quench rates are suggested. Also, for high-burnup BWR cladding applications, higher levels of Sn and Cr in Zircaloy-2 appear to be beneficial. For the high-burnup PWR application, reducing the tin level in Zircaloy-4 is shown to be beneficial. A superior in-PWR performance data (lower corrosion and lower irradiation growth compared to conventional Zircaloy-4) are presented for a Zr-Sn-Nb-Fe alloy.

Regarding the ex-reactor autoclave tests with good correlation to the in-reactor corrosion behavior, the following information is presented. For an indication of Zircaloy-2 corrosion

performance in BWRs, a long-term water test at 300°C appears to be more appropriate than the 520°C steam test. For an indication of corrosion performance of zirconium alloys in PWR, a 360°C water test (pure water or with 70 ppm lithium addition) gives better correlation than the 400°C steam test.

The in-pile tests in the PR loop at Halden indicate no acceleration of corrosion rate of Zircaloy-4 when the lithium level in coolant was increased at 4.5 ppm. This result contradicts the results of loop testing in France. In the past few years, conflicting results are reported in the literature regarding the effect of lithium in the coolant on the in-PWR corrosion resistance of Zircaloy-4. The results vary from no effect to a 30% corrosion acceleration. It is clear that more work is needed to determine conditions under which lithium accelerates the in-reactor corrosion rate of zirconium alloys.

A comparison of the corrosion behavior of a defective rod and adjacent nondefective rod irradiated for two cycles in a PWR indicates a significantly higher corrosion rate in the defective rod. This corrosion rate acceleration appears to be due to the hydride precipitates at the metal oxide interface in the defective rod.

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APPENDIX

LIST OF POSTER PRESENTATIONS 10TH ASTM ZIRCONIUM SYMPOSIUM BALTIMORE, MD; JUNE 1993

Hydride Characterization in Irradiated Zirconium Alloys

J. Thomazet – FRAGEMA, Lyon, France
F. Barcelo – Commissariat a l'Energie Atomique, Gif Sur Yvette, France
M. Trotabas
D. Gilbon
J. Y. Blank

Evaluation of Oxide Layer Thickness on Zircaloy-4 Tube by Electrochemical Impedance Spectroscopy

A. Frichet – PECHINEY, C. R. Voreppe, France
J. P. Mardon – FRAGEMA, Lyon, France
J. Senevat – ZIROTUBE, Paimboeuf, France

Correlation Study Among Corrosion Properties, Microstructure, and Additional Heat Input History of Zircaloy-2 Tubing

Y. Suzuki – Japan Nuclear Fuel Co., Kanagawa, Japan
T. Iwasaki
Y. Ito

X-Ray Small Angle Scattering of the Small Precipitates in Zircaloy

C. Miyake – Osaka University, Osaka, Japan
M. Uno
T. Kamiyama – Tohok University, Miyagi, Japan
K. Suzuki

Electron Spin Resonance Study of Oxide Films on Zircaloy Cladding

C. Miyake – Osaka University, Osaka, Japan
M. Uno
G. Abe

Magnetic Observation on Corrosion Susceptibility of Zircaloy Cladding

C. Miyake – Osaka, University, Osaka, Japan
G. Abe

M. Shimamoto – Nuclear Fuel Industry, Osaka, Japan
T. Kimura

Study on the Zirconium-Hydrogen System

S. Yamanaka – Osaka University, Osaka, Japan
K. Higuchi
M. Miyake

Observation on Corrosion Oxide Film Formed on Zirconium Alloy

T. Kimura – Nuclear Fuel Industry, Osaka, Japan
K. Kawanishi
M. Shimamoto
T. Okada

Interaction Between Factors Acting on the Uniform Corrosion Behavior of Zircaloy-4

D. Charquet – CEZUS, UGINE, France

Effect of Hydriding on Mechanical Behavior of Zircaloy-4 Structural Components of the Fuel Assembly Under Various Conditions

F. Prat – FRAGEMA, Lyon, France
J. Bard
E. Andrieu – Ecole Des Mines, Paris, France

Characterization of Post-Transition Corrosion Kinetics of Stress-Relieved, Recrystallized and Beta Quenched Zircaloy-4 Tubes

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Effects of Hydriding and Oxidizing on the Mechanical Properties of Unirradiated Zircaloy-4 Cladding Tubes

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Coralline Facility Study on Irradiation Behavior Under PWR Conditions of Zirconium-Based Alloys to be Used in the Fuel Assembly Structure

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Long-Term Out-of-Pile Corrosion of Zirconium Alloys

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Contribution of the Beta Flux to Corrosion Enhancement of Zr Alloys Under Irradiation

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Superimposed Effects of Grain Shape Anisotropy and Crystallographic Texture on Anisotropic Biaxial Creep of Zircaloy Cladding

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Mechanism of Oxidation of Zircaloy Fuel Cladding in Pressurized Water Reactors

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Evaluation of Non-Destructive Hydrogen Detection Methods in Zirconium Alloys

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The Ductile-Brittle Transition of Zircaloy-4 Due to Hydrogen

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Influence of Irradiation on Iodine Stress Corrosion Cracking Behavior of Zircaloy-4

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