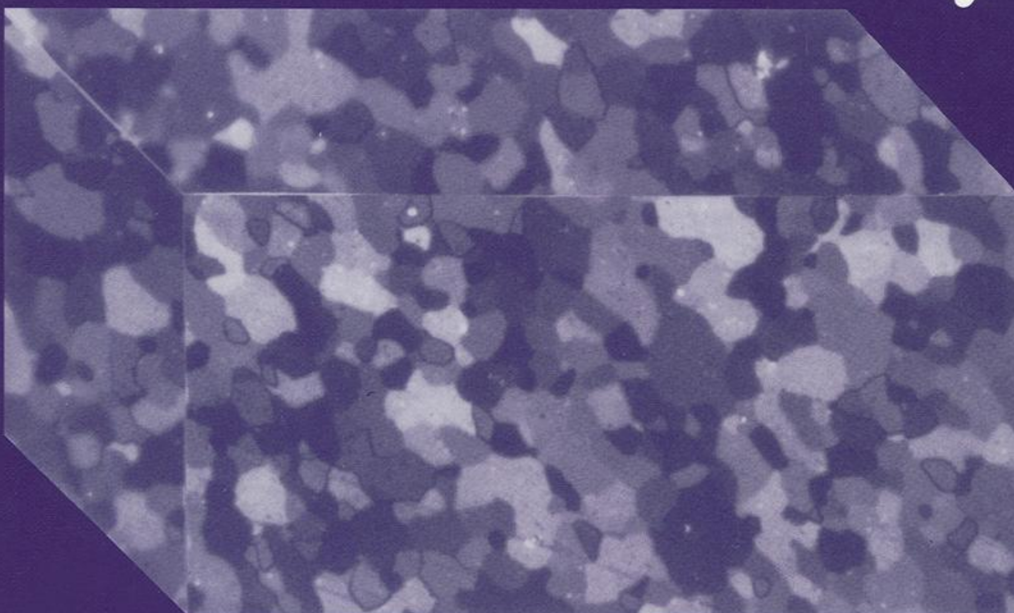
Zirconium in the Nuclear Industry



Ninth International Symposium

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Zirconium in the Nuclear Industry: Ninth International Symposium

C. M. Eucken and A. M. Garde, editors

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Peer Review Policy

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 editor(s), 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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Foreword

The Ninth International Symposium on Zirconium in the Nuclear Industry was held in Kobe, Japan, on 5–8 November 1990. The sponsor of the event was ASTM Committee B-10 on Reactive and Refractory Metals and Alloys in cooperation with the Japan Society of Newer Metals and the Japan Atomic Energy Society.

The symposium chairmen were C. M. Eucken, Teledyne Wah Chang, and Y. Mishima, Japan Society of Newer Metals. Serving as editors of this publication were C. M. Eucken and A. M. Garde, ABB Combustion Engineering Nuclear Power.

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Overview

This volume contains papers presented at the Ninth International ASTM Symposium on Zirconium in the Nuclear Industry held in Kobe, Japan, in November 1990. Zirconium alloys, especially Zircaloy-2, Zircaloy-4, and Zr-2.5Nb, have been the main materials used in the core of nuclear power plants since their first use in the early 1950s. Investigation of the behavior of zirconium alloys in these reactor environments and in laboratory tests designed to simulate particular aspects of the in-reactor environments has been a topic of continuing interest. This series of symposia, started in 1968 with a meeting in Philadelphia, has provided a forum for researchers to present their latest work to a body of their peers as a means of furthering technical understanding and interchange. The published proceedings of these symposia have gained a reputation as one of the most significant bodies of information on zirconium alloy behavior available in the literature. The Kobe symposium was attended by 204 participants from 17 countries.

Thirty-nine formal platform presentations and twenty-three poster presentations were given during the course of the symposium. The thirty-six platform presentations published in this volume underwent careful peer review and editing. The highlights of the discussions that followed each oral presentation and a listing of the titles and authors of the poster presentations are also included.

Because of the recent trends in the nuclear industry towards higher fuel discharge burnups for better fuel utilization, and higher heat ratings and coolant temperatures for better thermal efficiency, the technical interest in corrosion of zirconium alloys has increased significantly. Accordingly one topic that dominated the symposium was corrosion. Four separate sessions were devoted to aspects of zirconium alloy corrosion, and an invited paper presented during the opening session of the symposium summarized the results of an IAEA technical committee meeting held one year earlier. This invited paper focused on the report of an investigation into the effects of potential fields across the oxide film and the influence of alloy element valence on electron conductivity. The corrosion sessions addressed the effects of processing and alloying, corrosion mechanisms, modeling, effect of lithium hydroxide, and in-reactor corrosion performance. Non-corrosion related topics were discussed in a session devoted to fabrication and in two sessions devoted to mechanical properties of zirconium alloys. 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 generation of the nuclear energy.

Fabrication

Three of the papers in this session deal with specific details of cladding tube manufacturing, while the fourth describes the hot-working characteristics of Zircaloy-2 through construction of a processing map. Processing methods beneficial in minimizing the occurrence of microfissures in the pure zirconium liner and barrier cladding tube are described. These include use of a high Q factor, development of a small liner grain size, and the use of inner diameter pickling. A seven-variable model of the pilger process is shown to fit the data of the tube reduction process. A tooling design which produces increasing Q factor through the pass is shown to be beneficial to the development of the desired cladding tube texture. The Q factor of the final three passes correlates well with the contractile strain ratio of the product tubing.

Dynamic material modeling was used to generate a processing map for Zircaloy-2. The map shows a domain of dynamic recrystallization at 1013 to 1123 K and 0.01 to 2 s^{-1}. Instabilities are observed at less than 973 K and at strain rates greater than 1 s^{-1}. Since no similar studies of Zircaloy have been reported previously, this information offers considerable benefit to fabricators of Zircaloy products.

Mechanical Properties

Fracture toughness, creep, irradiation growth, and fatigue properties of zirconium alloys were the main topics of this session. The fracture toughness of Zr-2.5Nb pressure tubes was found to reach a minimum for hydrogen levels above 300 ppm. Fracture toughness of samples with radial hydrides show a very large dependence on hydrogen content up to 100 ppm and a small dependence above that level. When radial hydrides are present in material with 200 to 300 ppm hydrogen, a ductile-to-brittle transition occurs at 550 K. Another study found that post-irradiation fracture toughness of Zr-2.5Nb pressure tube material did not depend on initial tensile strength. The fracture mechanism is void formation and coalescence. The formation of fissures on the fracture surface governs the toughness.

A study of texture reorientation showed little change in texture during tensile deformation applied in the rolling direction, and large reorientations after high strains applied in the transverse direction. Mechanical properties and microstructures of Zr-Sn binary alloys were examined to evaluate the role of tin as a solid solution hardener and precipitation hardener. Iron-containing intermetallic precipitates in Zr-2.5Nb pressure tubing containing less than 500 ppm iron do exist, but they represent such a small volume fraction of the microstructure that they may not affect corrosion behavior or mechanical properties.

Strains generated by the stresses created at the oxide/metal interface due to oxide growth were found to be comparable to that of irradiation growth and these strains are accommodated by thermal creep. Biaxial creep tests on cladding produce prism slip in recrystallized material, but basal slip in cold-worked, stress-relieved material. Irradiation of this cladding decreased creep anisotropy due to activation of secondary slip systems. Independent studies of irradiation growth on Zr-2.5Nb pressure tubes showed that creep is more isotropic than assumed earlier. The threshold pressure at which iodine affects fatigue behavior was found to be higher than the pressure calculated to occur in BWR fuel rods. The fatigue limit was shown to decrease from 0.22% for unirradiated Zircaloy-2 cladding to 0.18% for material irradiated up to 6×10^{25} n/m^2 ($E > 1$ MeV).

Corrosion–Effect of Processing and Alloying

Control of alloy elements to a narrow range within the specification limits for Zircaloy-2 result in reduced sensitivity of uniform, ex-reactor corrosion on processing parameters. The controlled composition material, low tin content and high iron and chromium content, exhibits better corrosion resistance than nominal composition Zircaloy-2. Statistical analysis of the process variables in Zircaloy-2 cladding tube production shows that low tin content, texture characterized by high f_r values, stress relief annealing at final size, and the use of low intermediate annealing temperatures (especially late in the process) produce the best corrosion resistance to 773 K steam autoclave tests. The use of an accumulated annealing parameter to characterize the nodular corrosion resistance of Zircaloy-2 cladding tubes was questioned in another paper. The percentage cold reduction performed during each pilger mill pass was found to be more significant than the annealing parameter. The use of an electron microprobe with automated stage control was shown to be a useful means of relating the uniformity of alloy element concentration to 773 K autoclave corrosion resistance.

Tin was confirmed as the most important alloying element in determining uniform corrosion resistance during development of a new cladding alloy, Zr-1Sn-0.28Fe-0.16Cr-0.1Nb-0.01Ni. Another alloy development program concluded that the corrosion resistance of Zircaloy-4 could be improved by reducing tin content to 0.5% and adding a small amount of niobium to the alloy. Additions of Mo and V can be used to improve the mechanical properties of this alloy. These additions increase intermetallic precipitate density, but not the precipitate size. Other researchers saw little or no effect of iron, chromium, nickel, or oxygen content on uniform corrosion resistance of Zircaloys. Improved corrosion resistance with reduced tin content was attributed to a decrease in stress within the oxide.

Corrosion–Mechanisms

Results of several different types of analyses on oxide layers led to a barrier layer concept. The dense barrier layer changes when the oxide thickness reached 3 μm. The post-transition corrosion rate correlates with the properties of this barrier layer. Fine, equiaxed monoclinic oxide, which forms under the influence of hydrogen, cracks easily at grain boundaries and results in nodular corrosion. The use of Raman spectroscopy revealed the existence near the oxide-metal interface of tetragonal oxide which limits the corrosion kinetics prior to transition. At transition the tetragonal oxide decomposes to a porous monoclinic oxide in which grain boundary diffusion predominates. Raman spectroscopy revealed the presence of tetragonal oxide on Zr-Sn-(Fe, Cr, or Ni) alloys in addition to the monoclinic oxide observed in binary Zr-Sn alloys. Oxides of these alloys were shown to have the characteristics of n-type semiconductors by photo-electrochemical measurements. The addition of Fe, Cr, and Ni to Zr-Sn alloys increases the oxygen vacancy density in sub-stoichiometric oxide.

Atom probe measurements reveal the matrix of cladding to be fully depleted after only short time annealing, which implies that the alloy elements are all present in the form of intermetallic particles. The existence of a critical ΣA value for obtaining good uniform corrosion resistance is not related to changes in the matrix composition. Alloys exhibiting the highest electrical resistivity in the metal also exhibited the best corrosion resistance. The effect of beta quenching is to increase the solute concentration in the metal and thereby increase the electrical resistivity. Zirconium intermetallic compounds were shown to be electrochemically noble to the matrix. A model combining the passivity of the intermetallic particles and the fracture behavior of the oxide formed in autoclave tests was used to describe both uniform and nodular corrosion.

Corrosion–Modeling and Lithium Effects

Heat flux was shown to have a greater influence on corrosion rate acceleration than the thermal gradient across the oxide film only. When all the current corrosion models are examined in detail, the need for an improved model is still evident. Precipitation of hydrides at the metal-oxide interface reduces the coherency between the barrier layer and the base metal. As a result, both the oxidation rate and the hydrogen uptake by the metal increase after hydride precipitation in the metal.

The corrosion of Zircaloy-4 is accelerated when lithium hydroxide is present above a minimum value. Niobium-containing alloys are especially sensitive to this lithium enhancement. In concentrated LiOH, the presence of Li_2O prevents the growth of columnar oxide leading to the formation of a porous oxide film. Boron is shown to have an ameliorating effect on the corrosion rate of Zircaloy-4 in LiOH solutions, but at least 10 ppm boron is required to produce this effect. Less lithium is incorporated into the oxide when boron is present in the solution. Lithium and boron concentrations typical of start-of-cycle PWR coolant do not affect the corrosion rate of Zircaloy-4. Specimens corroded in LiOH solutions all show enhanced electronic conductivity in the oxide. Local dissolution of the oxide in LiOH solutions can generate porosity in pre-transition oxide films.

Corrosion–In-Reactor

Oxides formed in high-oxygen water exhibit a much thinner barrier layer than those formed under low oxygen conditions, which means that oxygen excursions can be very detrimental to corrosion resistance. In Zr-2.5Nb, oxide forms in ridges along the β-Nb phase. Nodular corrosion in BWRs correlates with average precipitate size and temperature. An additional acceleration factor in BWR nodular corrosion is embrittlement of the metal by hydrides, forming cracks just below the oxide-metal interface. Amorphous oxides are seen to form after columnar oxide grains. The amorphous oxide is considered to be an effective barrier to hydrogen penetration. One model containing a corrosion parameter that is an exponential function of burnup correlates well with the maximum oxide thicknesses observed in-reactor. A causal relation between precipitate size and corrosion performance has not been established, but the Second Order Cumulative Annealing Parameter fits the data better than the commonly used annealing parameter, ΣA. New alloys irradiated in PWR have shown both very good and very poor corrosion behavior in comparison to Zircaloy-4, and the corrosion behavior is a strong function of the alloy processing history. The corrosion-resistant alloys are being used in the form of duplex cladding tubes in order to circumvent the mechanical property disadvantages they exhibit.

Amorphization of intermetallic precipitates occurs during irradiation by neutrons, ions, and electrons. A model was developed to describe the damage sequence under these three types of irradiation to produce chemical disordering and, in the case of neutron irradiation, departure from stoichiometry.

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