Foreword

This publication, Zirconium in the Nuclear Industry: Twelfth International Symposium, contains papers presented at the symposium of the same name held in Toronto, Canada, on 15–18 June 1998. The sponsor of the event was ASTM Committee B-10 on Reactive and Refractory Metals and Alloys.

The symposium chairman was George P. Sabol, Westinghouse Electric Company (retired), and the editorial chair was Gerry D. Moan, AECL. The editors of this STP were George P. Sabol and Gerry D. Moan.
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Overview

The 12th ASTM International Symposium on Zirconium in the Nuclear Industry, held in Toronto, 15–18 June 1998, was attended by 230 engineers and scientists interested in the processing, use, and properties of the metal and its alloys. Seven sessions were devoted to the presentation of 41 peer-reviewed papers, and one poster session allowed detailed discussions of 30 poster displays. In addition, three presentations summarizing some of the history of the metallurgy and use of Zr alloys were invited from the recipients of the Kroll Award (R. B. Adamson, GE, USA; D. Charquet, CEZUS, France; and C. E. Ells and A. Sawatzky, AECL, Canada). The papers presented in the seven sessions at the Symposium and at the Kroll Award Luncheon are included in this publication.

The technical sessions covered topics ranging from the properties and behavior of Zr alloys at high irradiation fluences to the effect of oxide properties on the oxidation and hydrogen pickup rates. The session co-chairs and some highlights are as follows:

1. Properties at High Irradiation Fluences. R. B. Adamson and M. Limback: New Zr-based alloys containing niobium or tin or both are being developed with superior resistance to in-reactor corrosion and deformation. There were no unpleasant surprises in the deformation and microstructure studies of the Zircaloy and of Zr-2.5Nb at high fluences. These papers were important because they provided data from measurements of properties after irradiation to very high fluences and showed that the properties were those expected from tests carried out on material irradiated to lower fluences.

2. Hydrogen and Temperature Effects. R. A. Holt and T. Okubo: The solubility limit of hydrogen was shown to have been increased in Zircaloy materials by neutron irradiation, and the evidence for a detrimental effect of high concentrations of hydrogen on the corrosion resistance of Zircaloy-4 continues to mount. Some of the premature failures in reactivity initiated accident (RIA) tests may have been prompted by microstructural effects caused by welding of the test samples and not by degradation of the material properties. Thermomechanical tests have provided data for high-temperature creep laws, burst criteria, and ductility studies of current and new alloys deforming under accident conditions.

3. Deformation and Fracture Studies. A. M. Garde and E. R. Bradley: Axial cracking in irradiated Zircaloy fuel sheath is being studied, and proposed mechanisms include delayed hydride cracking and corrosion hydride cracking. The latter mechanism is based on test results that indicate the failures require simultaneous corrosion of the Zircaloy material. There appears to be a crack size effect on the crack growth resistance curves for irradiated Zr-2.5Nb material with high fracture toughness. The localization of deformation into slip bands in irradiated material has been shown to facilitate the initiation of iodine-induced stress corrosion cracking. Hydrogen present in Zr alloys induces an increase in the work-hardening rate and in the out-reactor creep resistance.

4. Processing and Alloy Development. M. Perez and C. Eucken: A new fabrication route using high pilger reductions up to 90% was summarized, and models that can be used to design improved pilger tools for better productivity and surface finish were described. In the processing of Zircaloy materials, it was shown that most precipitate growth occurs during the α-annealing stages, that the particle size distributions are mostly bimodal, and that materials with lower Sn concentrations have broader particle size distributions. Optimization
work on new alloys suggests that carbon concentrations should be kept below 100 ppm for improved corrosion resistance and that sulfur can improve the in-reactor creep resistance. The in-reactor corrosion resistance of the Zr-1Nb alloy is reported to be very good in PWR coolant with less than 5 ppb oxygen and in the absence of sub-cooled boiling; however, it appears susceptible to nodule formation when about 20 ppb oxygen is present in the coolant. Work on the effect of dilute additions of Mo, Nb, or V to zirconium showed that the best corrosion resistance was obtained in out-reactor tests when there was a critical concentration of solute atoms in the matrix and a set of second phase particles with sizes in a desired range.

5. Effect of Composition and Microstructure on Corrosion. D. Franklin and B. Cheng: Low tin concentrations in Zircaloy-4 containing less than 40 ppm nitrogen were found to increase the corrosion resistance in out-reactor tests by promoting the formation of a thicker tetragonal ZrO₂ layer. Tests also indicated that there was a benefit from using Zircaloy-4 material with Fe and Cr concentrations above the ASTM range, and that this benefit is as significant as that due to tin reduction within the specified range. Work on Zr alloys containing Fe and Cr showed that the Fe improved the out-reactor corrosion resistance, but could lead to the formation of cracks in the oxide and to the pickup of a high fraction of the hydrogen produced by the corrosion reaction. The major benefit of Cr is to minimize the hydrogen pickup. In Zr-2.5Nb material the effect of the Nb in the α- and β-phases has been studied, and the improved corrosion resistance has been found to be associated with a reduction in the Nb concentration in the α-phase because of the precipitation of β-Nb. A study of the corrosion and hydrogen pickup by Zircaloy-2 in BWRs showed that they could be improved by increasing the number of second phase particles with a diameter larger than 50 nm and lowering the Fe/Cr concentration ratio in the particles. Other similar work showed that the improved corrosion resistance from the α + β heat treatment of the outer shell of BWR cladding was associated with the presence of small particles and with their rapid dissolution during irradiation.

6. Corrosion Simulation and the Effect of the Environment. P. Rudling and F. Garzarolli: Work with high energy electron irradiation of Zircaloy-2 and Zr-2.5Nb samples showed that the microstructures produced by irradiation damage were similar to those produced by neutron irradiation. In Zr-2.5Nb both electron and neutron irradiation damage enhanced the precipitation of β-Nb and had similar effects on corrosion. However, in Zircaloy-2, the electron irradiation had no effect on the corrosion rate nor on Fe diffusion from the intermetallics. Studies of Zircaloy-2 corrosion in a BWR loop showed increased uniform and nodular corrosion caused by β and γ irradiation. The effects of lithium and boron continue to be studied, and both are observed to penetrate the oxide even to the inner protective oxide.

7. Effect of Oxides on Oxidation and Hydrogen Pickup Rates. B. Cox and C. Lemaignan: The effects of the electrical properties of the oxides on the oxidation and hydrogen pickup were studied, and in one paper it was shown that, in out-reactor tests, Zircaloy-4 with large precipitates and a high Fe concentration had a lower hydrogen pickup and an oxide with a lower electrical resistance than the corresponding material with a low Fe concentration and small precipitates. In another study examining Zircaloy-2 cladding after irradiations in a BWR reactor, it was found that materials with lower electronic conductivity had better corrosion resistance. In other papers it was considered that large second-phase particles and inclusions may serve as preferred pathways for hydrogen ingress, thus facilitating pickup of corrosion produced hydrogen. The long-held hypothesis of an inner barrier layer that controls oxidation and hydrogen pickup is confirmed by various methods of oxide characterization.

Nearly half of the papers presented were concerned with the corrosion and hydriding of different Zr alloys and the results presented reinforce trends started before the 11th Sym-
posium. The techniques used to characterize the oxides and their microstructures and properties have become very advanced. The industry, including the producers and users, is expecting that the work will lead to important conclusions about alloy development, about optimization of the processing parameters, and about station operating procedures so that the current and new Zr materials will continue to operate reliably to very high neutron fluences.

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