Discussion Section

This section contains written discussions to 36 of the 40 papers in this publication. The questions and answers that follow originated at the Eighth International Symposium on Zirconium in the Nuclear Industry after the presentation of each paper. Before the end of the symposium, the discussers were asked to write their questions, which were then sent to authors. These questions and the authors written responses comprise the section that follows.

The order of the discussions is the same as the Contents of this publication. The page numbers of the article being discussed appear at the beginning of each discussion.

Behavior of Pressure Tubes

Corrosion and Hydriding of N Reactor Pressure Tubes—DENNIS D. LANNING, A. B. JOHNSON, JR., D. J. TRIMBLE, AND S. M. BOYD, pp. 3–19.

B. Cox (AECL)—Results presented for early surveillance tubes from N reactor showed more symmetrical oxide thickness and hydrogen peaks (with respect to the flux profile) than the data presented today, which were more skewed towards the outlet end of the tube. Have the shapes of the oxide and hydrogen peaks changed with increasing exposure time, or is this apparent difference a result of more data points being taken on recent tubes?

D. J. Trimble—The skewed oxide thickness and hydrogen content profiles have been observed for the last four or five tubes examined (1165, 1054, 2755, 2954, and 3053). The apparent differences from previous tubes are probably due to more data points, but may also be the result of the developing thick oxide.

M. Noe (IAEA)—In the axial distribution of oxide thickness, out of flux values near the inlet and close to the outlet are very similar although these surfaces are subjected to coolant at 200° and 280°C, respectively. However, there is a high oxidation cusp in the areas under flux.

(1) Should it be concluded that flux has a specific effect different from the temperature effect on corrosion?

(2) Was there heavy crud in the areas under flux, which could be responsible for this enhanced corrosion?

D. J. Trimble:
Differences between out-of-flux oxide thickness near the inlet and outlet ends of the tubes were small (compared to differences between in-flux and out-of-flux values) but significant. Oxide growth rates at the out-of-flux positions are shown in Fig. 4 in comparison to the Hillner correlation for out-reactor oxidation. There is good agreement with Hillner's prediction at the inlet and outlet temperatures.

(1) Yes, there is a very significant flux effect different from the temperature effect. Factors of 20 to 60 enhancement attributed to flux were seen at given temperatures.

(2) There was a porous, iron rich crud layer of 10 to 20 μm, but we expect no effect of the crud. The heat transfer at this surface was quite low (10 to 15 W/cm^2), and there was no obvious corrosion species in the coolant that would concentrate in the crud (for example, LiOH).

A. M. Garde (Combustion Engineering)—Did you measure the hydrogen absorption fraction, and did it depend on the oxide thickness?

D. J. Trimble—The hydrogen absorption fraction in the flux zone of the N reactor pressure tubes is difficult to assess because of the azimuthal redistribution of the hydrogen. No systematic studies have been made to evaluate its dependence on oxide thickness.

B. F. Kammenzind (Westinghouse-Bettis)—Do you have an explanation for the peak in hydrogen concentration observed at the 2-m axial position of the tubes examined?

A. B. Johnson, Jr.—The upstream out-of-flux hydriding peak on the N reactor pressure tubes has not been accompanied by accelerated oxidation, contrary to the in-flux hydriding peak. The following reactor characteristics seem relevant to an explanation of this observation:

• Carbon steel spacers at both upstream and downstream out-of-flux locations (upstream spacers are nonprefilmed; downstream spacers were filmed during prior service in the upstream location).
• A large axial temperature gradient: ~200°C at the tube inlet; ~280°C at the tube outlet.
• A tendency for more damage to tube inner surfaces near the inlet during fuel charging operations.
• A prefilm oxide (2 to 4 μm) that was at or near transition when the tubes were installed.

The steel spacers in contact with the Zircaloy tubes offer the prospect of a cathodic hydrogen charging mechanism. The situation is exacerbated in the upstream end of the tubes by (a) rapid initial corrosion of the unfilmed spacers, (b) mechanical damage to the tube surfaces, and (c) slower healing of oxide damage and porosity at the low temperature compared to the higher outlet temperature.

K. Balarama Moorthy (Hyderabad Nuclear Fuel Complex):

• What is the pre-metallurgical condition of the tubes?
• Do you expect any difference in oxide film thickness buildup with respect to initial cold work of tubes, and the initial autoclaved layer?

D. J. Trimble:

• The tubes were cold worked to three different levels: 18, 30, and 35%. They were then autoclaved at 425°C for 72 h. The autoclave film thickness was 2 to 4 μm.
• No significant differences in oxidation rates have been observed for the different cold work levels.
• If significantly different prefilms had been applied, differences in oxide thickness buildup would be expected for in-flux exposures. Thinner prefilms would result in lower initial in-flux oxidation rates and therefore less overall oxide thicknesses after extended exposures. The thicker prefilms allow the oxides to reach the thick-film threshold more quickly, resulting in significantly thicker oxides after extended exposure.

V. Urbanic (AECL)—Has any hydrogen been detected in the helium gas surrounding the pressure tube, which could potentially contribute to hydrogen uptake of the tubes but from the outside as opposed to the inside of the tube?

D. J. Trimble—Although measurement methods have not been sufficiently sensitive to measure it, low levels of hydrogen are expected in the reactor gas. To assure that gas-side hydriding does not occur, the moisture content in the helium is maintained above a threshold that should assure maintenance of protective outer surface oxide film. Surveillance measurements of the surface oxide have confirmed this.

Oxidation and Deuterium Uptake of Zr-2.5Nb Pressure Tubes in CANDU-PHW Reactors—

VINCENT F. URBANIC, BRIAN D. WARR, ANGELA MANOLESCU, C. K. CHOW, AND MICHAEL SHANAHAN, pp. 20–34.

A. B. Johnson, Jr. (Battelle Northwest)—Occasionally, Mother Nature operates in our favor, for example, for Zr-2.5Nb, radiation-induced aging causes decreases in in-reactor corrosion. This was demonstrated in a study that you and I co-authored [1] and is further demonstrated by your recent work. Recognizing that there are differences in metallurgical condition for the earlier and later materials, do you see similarities in radiation effects on the microscopy?

V. Urbanic—Despite the differences in metallurgical condition, there are some similarities in the effects of radiation on the microstructure. In the early material, which was beta quenched and aged (with some intermediate cold work), irradiation produced additional βNb precipitation along twin boundaries in the α'Zr structure, over and above that produced during the initial aging treatments. For the cold-worked material described here, irradiation is seen to have caused precipitation of βNb precipitates within the elongated alpha Zr grains; these precipitates are not present in the as-fabricated structure prior to irradiation.

Bo Cheng (General Electric)—Your data showed that the low hydrogen uptake of Zr-2.5Nb may be associated with its lower corrosion rate in the CANDU-type reactors. Can you compare the difference of the hydrogen pickup fractions of Zr-2.5Nb and Zircaloy-2 in CANDU reactors? Why are the pickup fractions in CANDU reactors much higher than in the PWRs and BWRs and even laboratory tests?

My second question is on the corrosion variability of Zircaloy-2. It is well known that Zircaloy corrosion is highly dependent of manufacturing variables in the laboratory, and also in light-water reactors. Have you seen from component examinations or test programs whether manufacturing variables may influence the corrosion behavior of Zircaloy-2 in the CANDU-type reactors?

V. Urbanic—In CANDU reactors the theoretical uptake from waterside corrosion is in the range of 30 to 60% for Zr2 pressure tubes, whereas for all Zr-2.5Nb pressure tubes, except Tube P3L09, the calculated uptake fraction is generally in the low end of the range 5 to 20%. The percentage uptake for Zr2 is consistent with that seen in most PWRs and laboratory tests. Uptake fractions however are higher than in BWRs because of the more oxidizing water chemistry in those systems compared to that in CANDU. In response to your second question, manufacturing variables do not seem to account for the variability in corrosion of Zr2 pressure tubes in Pickering Units 1 and 2, since all pressure tubes for both those units were fabricated to the same specification.

Evaluation of Zircaloy-2 Pressure Tubes from NPD—CHRISTOPHER E. COLEMAN, BRIAN A. CHEADLE, ALLAN R. CAUSEY, PETER C. K. CHOW, PAULINE H. DAVIES, MURRAY D. MCMANUS, DOUGLAS K. RODGERS, STEFAN SAGAT, AND GARY VAN DRUNEN, pp. 35–49.

E. Tenckhoff (Siemens)—The phenomenon of "toughness" was described qualitatively by micro-fractographs. Is there also a quantitative definition for the ductile-brittle transition? What are the reasons for choosing K_{IC} values of approximately 60 to 70 MPa $\cdot$ m$^{1/2}$ in the definition of this transition value?

C. E. Coleman—The brittle-ductile transition of the Zircaloy-2 pressure tubes from NPD was primarily indicated from the load-displacement curve of the fracture toughness tests on compact specimens. Specimens tested at low temperatures had little deviation from a straight loading line up to fracture and were called "brittle" while specimens tested at high temperatures exhibited increasing crack growth resistance with cracking and were called "ductile." The microfractography confirmed the macro-behavior with the transition value being 60 to 70 MPa · m$^{1/2}$.

K. Balarama Moorthy (Hyderabad Nuclear Fuel Complex)— Did you carry out conventional Charpy impact tests to determine ductile-brittle transition temperature? If so please give some details.

C. E. Coleman—We have done no impact tests on pressure tubes from power reactors. We now have an instrumented Charpy machine in our protective cells and the correlation work between fracture toughness, as measured from compact specimens, and miniature impact specimens is about to begin.

Growth, Fracture, and Nondestructive Evaluation of Hydride Blisters in Zr 2.5 wt% Nb Pressure Tubes—MARC LEGER, G. D. MOAN, A. C. WALLACE, AND N. J. WATSON, pp. 50–65.

B. Cheng (GE)—You showed data on the crack depth of hydride blisters measured by ultrasonic testing. With all the hydride blister experiences you have with CANDU reactors, have you developed or attempted to develop nondestructive techniques for detection of hydride blisters (not cracking) in reactor components? If yes, what types of techniques are you working on?

M. Leger—Blisters are only detectable in-situ by ultrasonics. The evidence strongly indicates that the cracks are being imaged in pulse-echo mode, and uncracked blisters are not detectable. Recently, there is evidence that some shear wave velocities in blisters are more affected than others, offering a potential testing technique.

B. F. Kammenzind (Westinghouse-Bettis)—(1) Neglecting the two phase region, did the size of the blister grow faster with thermal cycling or in the steady-state case?

(2) From your data were you able to estimate the size of the hysteresis between the precipitation and dissolution solvus of the hydrides at your operating conditions?

(3) Were your observed blisters the epsilon or delta phase of the hydrides?

M. Leger—(1) The zone of very dense hydride is smaller in the thermally cycled blisters than in the steady-state case for an equivalent time at high temperature. (Figures in the paper illustrate the effects).

(2) We did not estimate the difference from this work. We used data available in the literature for Zircaloy and estimated the precipitation TSS for Zr-2.5 Nb based on measurements from dissolution experiments. These estimates produced a good fit to the observations. The hysteresis is large with the difference in temperature of the limits on dissolution and precipitation being about 60°C for 70-ppm hydrogen samples.

(3) All measurements done to date (X-ray diffraction, plasmon loss in EELS, Nuclear Reaction Analysis of deuteride composition) indicate that it is delta.

E. J. Savino (Comision Nacional de Energia Atomica–Argentina)—Can you completely correlate the blisters observed in the G16 tube of Pickering 2, which failed in 1983, with blisters grown in the laboratory?

M. Leger—The correlation so-far is limited to the observation that blister "E" (one of the blisters at the crack initiation site in G16) would fit very close to the mean line of the figure of profile height versus cracking stress at 90 MPa (outlet operating stress in Pickering 2). The blisters on G-16 were larger than those found on other tubes.

E. Hindle (UKAEA)—Have you seen any hydride blisters on reactor pressure tubes that have not been in contact with cold surfaces?

M. Leger—No we have not. In fact, Zr-2.5 wt% Nb pressure tubes that have been in contact with calandria tubes in reactor and were removed for examination, have not contained any blisters. The hydrogen equivalent levels at the contact areas have been relatively low.

Effects of Hydride Morphology on Zr-2.5Nb Fracture Toughness—ANDREW C. WALLACE, GORDON K. SHEK, AND OLEV E. LEPIK, pp. 66–88.

A. B. Johnson, Jr. (Battelle Northwest)—Have you performed parallel studies on Zircaloy-2? If so, how do the trends compare to Zr-2.5Nb?

A. C. Wallace—Figure 1 of the paper provides data for Zircaloy-2 with radial hydrides at various hydrogen concentrations and HCC values. Direct comparisons with the Zr-2.5Nb data are hampered by the fact that the same hydride morphologies and hydrogen concentrations have not been tested for both materials. However, the general trends are quite similar. Comparisons at about 60-mg/kg hydrogen and HCC from 0.5 to 0.6, suggest a slightly higher toughness transition temperature for Zr-2.5Nb, and the transition for Zr-2.5Nb occurs over a narrower temperature range. Lower shelf toughness is comparable for both materials, while the upper shelf values appear slightly higher for Zr-2.

Effects of Loading and Thermal Maneuvers on Delayed Hydride Cracking in Zr-2.5 wt% Nb Alloys—GORDON K. SHEK AND DAVE B. GRAHAM, pp. 89–112.

Dr. Abraham D. Banchik (Comision Nacional Energia Atomica-Argentina)—I would like to know how you changed the hardness of your specimens.

G. K. Shek—Details of specimen preparation to obtain different hardness is given in the paper. This is mainly done by subjecting Zr-2.5Nb extrusions to different thermomechanical treatments such as stress relief, cold work, and intermediate anneal.

Brian Cox (AECL)—Your micrograph of the specimen that had the load reduced during DHC showed that the load reduction induced a cluster of hydrides to form, instead of the usual single highly oriented hydride at the crack tip. The volume change caused by the precipitation of this cluster of hydrides would be significant and would result in an additional reduction in the local stress at the crack tip. The effect of this hydride precipitation could be large, depending on the aspect ratio of these hydrides. Have you included this effect in your calculations of the effects of partial unloading of the specimens?

G. K. Shek—The finite-element elastic-plastic stress analysis has not taken into account the effects of crack-tip hydride precipitation on stress distribution. You are certainly right that the stress that arises from hydride precipitation could be significant because of the large difference in volume between the hydride phase and the matrix. This stress may also be important in understanding K_{IH}, the threshold stress intensity for hydride cracking and its relationship with the fracture toughness of hydride. We are considering to model the effect on stress by precipitation of a single hydride at the crack tip.

Edward Hindle (United Kingdom Atomic Energy Authority)—Can you comment upon the difference in the delayed hydrogen cracking behavior of Zr-2.5Nb compared with that of Zircaloy-2?

G. K. Shek et al.—The threshold stress to initiate hydride cracking K_{IH} is on the average higher in Zircaloy-2 than Zr-2.5Nb pressure tube, probably because of the matrix strength. It is also known that the diffusion coefficient of hydrogen is higher in the two phase Zr-2.5Nb alloy than in Zircaloy. This together with the strength effect on crack velocity suggested that DHC velocity will be higher in Zr-2.5Nb than that in Zircaloy pressure tube.

Corrosion I

Influence of Chemical Composition on Uniform Corrosion of Zirconium-Base Alloy in Autoclave Tests—CRAIG M. EUCKEN, PETER T. FINDEN, SIEGRUN TRAPP-PRITSCHING, AND HANS G. WEIDINGER, pp. 113–127.

A. B. Johnson, Jr. (Battelle Northwest)—(1) Our results from ETR G-7 Loop tests suggested that in some materials factors that influence oxidation are not the same as those that influence hydriding. Are data for hydriding trends available? If so, do they consistently parallel the oxidation results?

(2) Comparison of oxidation of three Zircaloy-2 lots in-reactor and at 400°C in steam indicated a reversal of the oxidation order-of-merit, suggesting that steam autoclaving is not satisfactory to predict in-reactor oxidation behavior. Results from your study show differing results for steam (400°C) and water (350°C). Do you have a basis to suggest which autoclaving medium correlates best with reactor data?

F. Garzarolli—(1) We do not yet have results from long enough exposure times to answer this question. First results from specimens analyzed after an exposure time of about 400 days at 350°C do not indicate significant variations in relative hydrogen pick up.

(2) Autoclave tests of archive samples indicate that the 350°C water tests are more relevant for the PWR fuel rod corrosion than 400°C steam tests. However, other details of the testing are also of importance, as shown in paper 17 (Microstructure and Corrosion Studies for Optimized PWR and BWR Zircaloy Cladding by F. Garzarolli et al. pp. 202–212 of this volume).

G. P. Sabol (Westinghouse)—(1) Are you doing corrosion tests, and do you have any data on corrosion in lithiated solutions?

(2) Are there differences in cold workability as the (Fe + Cr) increases from the 0.2 to 1% levels?

F. Garzarolli—(1) The 49 lots discussed here are also being studied in lithiated solution, but these tests are not yet finished.

C. Eucken—(2) The Type III materials are the only ones that span this wide range of total iron plus chromium content, and these materials were not cold worked. We observed extremely slight differences in fabricability for these alloys during hot rolling. Based on observations of these alloys and on other alloys not described by this paper, we conclude that fabricability degrades significantly only when iron content is above about 0.5% or when chromium content is above about 1.5%.

B. F. Kammenzind (Westinghouse-Bettis)—You indicate that decreasing the tin content increases the nodular corrosion performance in a 500°C steam test. Do you know if the number density of nodules is decreasing or is the size of the nodules decreasing?

F. Garzarolli—Nodular corrosion was only estimated by weight gain measurements in this case.

B. Cheng (GE)—You prepared specimens using two different cooling rates. What is the effect of cooling rate on the uniform oxide growth transition and post-transition oxide growth rate? Is alloy chemistry more important than cooling rate, or are both factors equally important in controlling the uniform oxide growth?

F. Garzarolli—The effect of chemistry on uniform corrosion is much larger than the effect of the rate of beta-quenching in the range studied here. In general, an increasing quenching rate was found to reduce post-transition corrosion and to increase time-to-transition slightly.

Correlation Between 400°C Steam Corrosion Behavior, Heat Treatment, and Microstructure of Zircaloy-4 Tubing—TOMAS THORVALDSSON, THOMAS ANDERSSON, ANDERS WILSON, AND ANTONY WARDLE, pp. 128–140.

R. M. Kruger (GE)—The precipitate size distributions, coupled with measurements of precipitates per unit volume, should yield estimates of the percentage of solute that is precipitated. Is most of the solute precipitated in *all* of the cases considered here? If so, how could the small, residual amounts of unprecipitated solute explain the wide variations in weight gain?

T. Thorvaldsson—Most of the chromium and iron are certainly precipitated out in intermetallic particles. The exact remainder in solid solution is not easily possible to access by TEM techniques since exact particle shape, exact number density, and so forth must be measured. Nobody so far has managed to do this in a quantitative way.

Small amounts of solute in the parts per million (ppm) range can influence the corrosion properties, see for instance the influence of silicon. If this is the case for iron or chromium it is still too early to say, but we think it is a definite possibility.

M. Noe (IAEA)—Do you plan to check the order of merit of the different alloys, or alloys with different microstructure, as determined on the basis of the 400°C steam test, by performing a corrosion test at ≈350°C in water? This test is more representative of reactor conditions. It is suspected that this order could be modified.

T. Thorvaldsson—We consider the long-term 400°C steam test to be a good test even for a reactor behavior. Presently we are not performing 350°C water tests.

J. Harbottle (CEGB)—You conclude that within the narrow range of 6 to 12% the degree of recrystallization does not significantly influence the corrosion rate. Could you say what effect higher values of recrystallization are likely to have on corrosion rate?

T. Thorvaldsson—A fully recrystallized material has lower weight gains than a stress relieved, that is, partially recrystallized material. We suppose that a gradual change will occur as a function of recrystallization. Within a narrow range, as in normal stress relieving treatment, we consider that effect negligible. Other effects, such as the exact annealing parameter, are more important.

R. B. Adamson (GE)—How did you choose the activation energy used in the analysis ($Q \sim 65\ 000$)? Must a specific activation energy be used for each set of experiments conducted?

T. Thorvaldsson—The activation energy was chosen as the average value from data derived from 400°C steam autoclave tests at 10.0 MPa for 72 h. The full details are given in Ref *1*.

Ideally one set of data is sufficient. It is very important to keep within the same oxidation cycle when comparing data. This is an experimental difficulty.

Influence of the Manufacturing Process on the Corrosion Resistance of Zircaloy-4 Cladding—JOHN J. SCHEMEL, DANIEL CHARQUET, AND JEAN-FRANCOIS WADIER, pp. 141–152.

A. Strasser (S. M. Stoller Corp.)—Considering the variability in the structure of the TREX as a function of its cross section after beta quenching, what would you recommend as the acceptance parameters for a beta quenching process qualification to give uniform corrosion resistance?

J. Schemel—The tubing resulting from all of the process variations in this experimental program when given a final heat treatment typical of reactor application has shown uniformly good corrosion resistance. There seems to be no basis for being concerned about the beta quench process beyond the parameters used for years to assure a prompt transfer of the billet or bar to a water bath.

R. A. Holt (Ontario Hydro)—Is there a 1:1 correspondence between the in-reactor corrosion rate of a particular batch of tubing and that seen in the 400°C steam test?

J. Schemel—No. We can not claim such a correspondence. We found that the variability observed was random within and between lots, and no autoclave specimens were from actual tubes for which in-reactor oxide film thicknesses were measured. About 50 specimens from a large number of the same lots were tested in the autoclave and used for the comparison.

G. P. Sabol (Westinghouse)—What is the critical cooling rate below which the white oxide is avoided?

J. Schemel—A cooling rate slower than about 40 K/s is adequate to avoid the peculiar effect noted in this paper.

A Laboratory Method to Predict Hydriding Properties of Zirconium Alloys Under Irradiation—A. G. JOHNSON, I. S. LEVY, D. D. LANNING, F. S. GERBER, AND D. J. TRIMBLE, pp. 153–164.

H. S. Rosenbaum (GE)—Do you advocate use of the aqueous LiOH test in conjunction with another test for oxidation? According to your correlation of hydrogen uptake with oxidation rate, it would seem possible to have a relatively low hydrogen uptake, but in-reactor that same material could oxidize rapidly leading to high hydrogen uptake. Isn't that so?

A. B. Johnson—Figure 3 of the paper indicates that oxidation and hydriding trends were concomitant for all but one of the eleven tubes examined after service in the N reactor. Tube 2755 had the expected oxide thickness, but less-than-expected hydriding. This evidence indicates that oxidation and hydriding frequently track each other, but we have seen other exceptions, for example, Zircaloy-2 Lots AT, CT, and HT exposed in the ETR G-7 Loop. The exceptions we have observed involved both normal and relatively high oxidation rates, accompanied by low hydriding rates under irradiation. So ETR G-7 Loop Lot CT Zircaloy-2 specimens had the highest oxidation rates but lowest hydriding rates, contrary to your expectation. However, the Lot CT result underscores the validity of your basic point: that

oxidation and hydriding can go in different directions. Studies by other investigators seem to be centering on factors that influence oxidation. Our test offers an approach to improved understanding of the factors that influence hydriding. Combining those insights can preclude the need for separate tests.

B. Cox (AECL)—I can appreciate the advantage of the out-reactor LiOH rest for comparisons with the ETR-G7 loop results where operation was with LiOH. However, the N reactor has always run with NH$_4$OH. Have you done similar out-reactor tests with concentrated NH$_4$OH and high hydrogen overpressures to see if correlation with N-reactor tube results is better?

A. B. Johnson—The ETR G-7 loop operated with pH 10 LiOH when the coolant was oxygenated. For low-oxygen operation, pH 10 NH$_4$OH provided radiolytic hydrogen to facilitate low-oxygen operation. Three Zircaloy-2 lots had the same ranking for hydriding (HT>AT>CT) in the LiOH and NH$_4$OH G-7 Loop coolants. This ranking was reproduced in the concentrated LiOH autoclave test. You are correct that the N reactor coolant was ammoniated. Again, the LiOH laboratory test gave the right answer in eight of eight attempts, namely, that Tube 2755 had the lowest efficiency for hydrogen absorption, compared to other N reactor tubes that were removed for examination. So the lithiated laboratory test correlated with Zircaloy hydriding characteristics in lithiated and ammoniated reactor coolants.

Even so, your suggestion to investigate hydriding in concentrated NH$_4$OH may have merit.

M. Noe (IAEA)—Do you think that the corrosion test with concentrated LiOH could be used for this "ranking of merit" on other properties than hydriding, for instance for corrosion rates and, in some way, replace the 400°C test in steam?

A. B. Johnson—Three Zircaloy-2 lots exposed in the ETR G-7 Loop had the following rankings in the oxygenated coolant: CT>AT≃HT for oxidation; HT>AT>CT for hydriding [2]. The laboratory lithium hydroxide test reproduced the in-reactor hydriding ranking, but not the oxidation ranking.

R. B. Adamson (GE)—Do you feel the test will be useful for predicting hydriding in other types of reactors, such as commercial PWRs or BWRs?

A. B. Johnson—The test reactor hydriding rankings for three Zircaloy-2 lots (AT, CT, and HT) were similar in oxygenated (BWR-like) and hydrogenated (PWR-like) environments. The hydriding ranking in the lithium hydroxide test reproduced the in-reactor rankings for both oxygenated and hydrogenated reactor environments, providing preliminary evidence for relevance to zirconium alloy hydriding behavior in both BWRs and PWRs. However, further confirmation is required, indexed directly to known hydriding behavior in BWRs and PWRs.

J. Thomazet (Framatone Nuclear Fuel Division-FRAGEMA)—Do you have a good testing reproducibility in lithiated environment?

A. B. Johnson—Yes. Both for results on duplicate specimens in a given autoclave run and on a qualitative basis, from one autoclave test to another. The overall standard deviation for the hydrogen absorption efficiency in a given autoclave test was ±2.5%. From test-to-test, specimens from Tube 2755 had the lowest hydrogen uptake efficiency in eight autoclave runs, compared to other N reactor tubes.

V. Urbanic (AECL)—Exposures in concentrated lithium hydroxide solutions are accom-

panied by the formation of thick oxide films. In the analyses of these specimens for hydrogen pickup, did you remove the oxide before analyzing for hydrogen? Can you also comment on the need to remove the oxides before hydrogen analyses of zirconium alloys.

A. B. Johnson—The oxides on specimens autoclaved in the lithium hydroxide tests were in the range of 45 to 260 mg/dm^2. In most cases, we have left the oxides in place on specimens submitted for hydrogen analysis. In one case, we analyzed irradiated thick-film specimens (approximately 2370 mg/dm^2) for hydrogen with and without oxides in place (EPRI NP-5132, pp. 3–32). For the very thick oxides, approximately 20% of the total hydrogen appeared to be associated with the oxide film. However, for thinner oxides, there are indications that hydrogen associated with the oxides is a small fraction of the total.

G. P. Sabol (Westinghouse)—Can you recommend a temperature, time, and LiOH concentration for a screening test?

A. B. Johnson—Investigations to date suggest that acceptable combinations within a temperature/time/concentration field are defined by an oxidation rate (indicated in the paper) that results in deterioration of hydriding discrimination. We have not investigated the lower limit, but believe that it is defined by the lowest rates that are acceptable for timely completion of the test.

Development of a Mechanistic Model to Assess the External Corrosion of the Zircaloy Claddings in PWRs—PHILLIPPE BILLOT, PIERRE BESLU, ALPHONSE GIORDANO, AND JOEL THOMAZET, pp. 165–186.

B. Cox (AECL)—My understanding is that you varied the LiOH concentration and the pH independently in your CIRENE loop tests by varying the boric acid concentration. Do you have autoclave data that show an effect of boric acid in ameliorating the effects of concentrated LiOH similar to those reported by D. Tice (UKAEA, Springfield)? Did all your CIRENE loop tests contain boric acid as well as LiOH? If you had any tests with LiOH only, did they show similar effects of concentration of lithium under boiling conditions to the LiOH + H$_3$BO$_3$ tests?

P. Billot—Although the autoclave tests performed in a lithium hydroxide environment are not reproducible, they result in a sharp acceleration in corrosion, and in an increase of the fraction of hydrogen pick-up (60%). The addition of 10 ppm of boron as boric acid in a 0.2M solution as LiOH does not reduce the enhancement of Zircaloy corrosion observed in a solution of 0.2M of lithium hydroxide. With an addition of 10 ppm of boron, oxidation rates decrease by a factor of 2 to 3 and with 1000 ppm of boron, the corrosion kinetics are close to those obtained in pure water.

All the CIRENE tests were conducted with boric acid and (LiOH), except one test that was conducted under KOH + H$_3$BO$_3$.

No test without boric acid was performed in the loop until now. But since the lithium concentration at the wall depends on the water coolant pH, the effects of lithium concentration under boiling conditions will be certainly different.

L. Ramanathan (I.P.E.N. Brazil)—Is the two to three times increase in corrosion rate between specimens corroded in the autoclave and in the out-of-pile loop caused by differences in water chemistry or is it caused by the effect of increased transport of oxygen between interfaces?

P. Billot/J. Thomazet—An increase in the corrosion rate (two to three times) in out-of-pile loop is due to the effect of increased transport of oxygen in Zirconia under heat flux.

Chemistry is not responsible for the increase in this case but rather the autoclave environment.

Under boiling conditions, concentration of species, LiOH in particular, leads to an additional effect, and an increase in corrosion by a factor well superior to 3, depending on the ebullition rate, can occur.

Corrosion II

Lithium Uptake and the Accelerated Corrosion of Zirconium Alloys—NATESAN RAMASU-BRAMANIAN, NIC PRECOANIN, AND VICTOR C. LING, pp. 187–201.

G. P. Sabol (Westinghouse)—(1) It is not clear that anion vacancies in the oxide have much to do with the corrosion rate since most oxygen is transported down grain boundaries. Why do you make a point of the role of a greater concentration of anion vacancies in the oxide with lithium?

(2) We have done some work on lithium in ZrO_2 films and find leachable lithium as you report. We also found lithium after removal of the leachable lithium. We found no acceleration in LiOH solutions until the lithium in the lattice reached about 100 ppm. Did you observe any such correlation?

(3) A difference we found in the oxide films on samples corroded in pure water and in LiOH is that fine cracks extended to the metal/oxide interface in samples corroded in LiOH and were absent in the pure water exposed samples. This suggests that the mechanical properties of the oxide are effected by lithium in the oxide. Do you find similar effects?

N. Ramasubramanian—(1) I agree that anion vacancies in the oxide have a minor contribution to the corrosion rate during normal oxide growth. However, in concentrated alkaline (lithiated) solutions when the nonporous layer at the alloy-oxide interface is very thin, perhaps only the thickness of a nucleating crystallite, the concentration of anion vacancies in the oxide crystallite and its influence on oxygen diffusion may have to be considered.

(2) We have some data points to relate nonleachable lithium in the oxide to the corrosion rate. Yes, our finding agrees with yours. A minimum lithium content in the oxide appears to be necessary for acceleration in corrosion to occur. However, the amount of nonporous part of the total oxide has to be used to arrive at the concentration, in ppm units, of the lithium in the oxide.

(3) We have not observed cracks in the oxide as a unique feature distinguishing films grown in lithiated solutions. In the future careful examinations of the oxide cross sections have to be made before the acid etch to reveal the alloy-oxide interface.

K. Balarama Moorthy (Hyderabad Nuclear Fuel Complex)—(1) In the first slide projected, are the data on Zr-2.5Nb from the fuel tube or pressure tube?

(2) Can we positively say that the texture of the material does not have any influence on corrosion behavior during irradiation?

N. Ramasubramanian—(1) The data shown are for Zr-2.5Nb pressure tube material. (2) No, we cannot.

A. Strasser (S. M. Stoller Corp.)—Did you investigate the effect of vanadium in Zircaloy chemical composition (within ASTM specifications) on the corrosion behavior, or if not would you speculate on their potential effects in combination with lithium?

N. Ramasubramanian—We have not investigated systematically, the effect of Zircaloy composition on the corrosion behavior. The effect of undissociated lithium hydroxide, according to the mechanism we are proposing, is most pronounced on oxide crystallite surfaces. The size of the oxide crystallites is quite small compared to the grain size, and therefore, any effect of composition on corrosion in the presence of lithium is likely to be a minor one.

Microstructure and Corrosion Studies for Optimized PWR and BWR Zircaloy Cladding—
FRIEDRICH GARZAROLLI, ECKHARD STEINBERG, AND HANS G. WELDINGER, pp. 202–212.

B. Cox (AECL)—When looking at trends in post-transition behavior in long autoclave tests that involve a change in water chemistry, you should reverse the change and return to the original condition to show that the trends also reverse and return to the original relative behavior. If you do not do the complete cycle you cannot be sure that the trends you report would not have occurred anyway, since post-transition rates are not linear with time.

H. G. Weidinger—We of course agree with you, that for a systematic investigation of such a "change effect" one has to proceed as you say. Our finding came out of a long-range study of the influence of adding hydrogen to the water after long-term corrosion with hydrogen addition to answer some questions on how Zircaloy behaves in a practical situation like this. And we had to keep the hydrogen addition for a long time, so repeating the procedure was just practically not feasible. But nevertheless, we feel our finding is a useful contribution to the important question of what is a representative out-of-pile corrosion test.

H. H. Klepfer (Exec. Tech. Inc.)—How are compositional variations, within the ASTM specifications, reflected in your data? Are the effects within the scatter band of the data?

H. G. Weidinger—There was no systematic variation of the chemical composition of the Zircaloys investigated here. The contents of iron, chromium, nickel, and tin were in the normal range end of commercial Zircaloys. That also holds for carbon and oxygen. So you are right that the scatter of the data reflects the scatter of the chemical composition as mentioned.

R. B. Adamson (GE)—The critical values of A, which you report, are calculated based on a value of $Q = 80\,000$. Do you suggest that 80 000 is a universal number, independent of material chemistry, thermomechanical history, and so forth?

H. G. Weidinger—We are today using the Q/R value, 40 000, which corresponds to your figure. This value was first used (several years ago) to describe the recrystallization behavior and the strength dependency on A, but with a different constant C in the expression $C + \exp(-Q/RT)$, to be consistent with our previous publication. In addition, we are still working on a more mechanistic understanding of the Q/R value.

K. Balarama Moorthy (Nuclear Fuel Complex)—Please comment about the role of grain size and residual cold work in Zr2 and Zr4 fuel tubes on in-pile corrosion resistance.

H. G. Weidinger—In this study, we used Zircaloy with grain sizes in the commercial range only. It was shown that out-of-pile uniform corrosion increases with increasing strength (that is, residual cold work) in nonhydrogenated water, whereas in hydrogenated water the ranking of the corrosion rate followed the A factor. This latter effect is also found in-pile as shown.

V. Urbanic (AECL)—Can you comment on the apparent change in flux dependence that

is seen with the change in accumulated annealing parameter or, in other words, precipitate size.

H. G. Weidinger—There is some more data in the written paper that give evidence how we evaluated the flux and temperature dependency of these two types of corrosion. But we do not yet have a mechanistic explanation for these phenomena.

B. Cheng (GE)—(1) Your in-reactor and ex-reactor corrosion data show a qualitative correlation. Are those data produced on identical materials? How about the in-pile fuel rod data?

(2) Another question is the beta quench (or alpha + beta) history of all those samples. It is well known that the beta quench before processing is very important. Did your sample receive the same beta quench history?

H. G. Weidinger—(1) As you say, this is a qualitative comparison of in- and out-pile behavior, where identical samples are not necessary.

(2) Of course beta-quenching plays an important role. Our data refer to beta-quench rates as commercially used. Where "fast quenching" was indicated, the quenching rates were higher.

B. Cheng (GE)—In the Seventh ASTM Zirconium Meeting in France, there were papers that discussed the effect of precipitate size on the nodular corrosion in BWRs. Although it has been generally recognized that precipitate distribution (size or number density) can be correlated to the out-of-pile and, in some cases, the in-pile corrosion, there are deviations from the correlation. One such deviation is high alpha annealing. One can anneal Zry-2 at 700 to 800°C to grow very large precipitates and have a large accumulated annealing parameter, yet the nodular corrosion resistance becomes excellent. How do you rationalize this discrepancy in corrosion performance in terms of precipitate size or accumulated annealing parameters?

H. G. Weidinger—This paper tries to summarize the finding on uniform and nodular corrosion for parameters that are normally technically relevant. There are certain exceptions for extreme parameters where there is no in-pile verification.

G. P. Sabol (Westinghouse)—You report a good correlation of PWR corrosion with autoclave tests performed in hydrogenated water. Can you please report on the recommended range of hydrogen used in the autoclave? Are there critical upper or lower hydrogen overpressures?

H. G. Weidinger—The hydrogen content in the pressurized autoclave water was kept in the same range as it is in the PWRs, that is, 2 to 4 ppm.

Corrosion Performance of Zircaloy-2 and Zircaloy-4 PWR Fuel Cladding—PETER RUDLING, HAKAN PETTERSSON, THOMAS ANDERSSON, AND THOMAS THORVALDSSON, pp. 213–226.

R. B. Adamson (GE)—Can you comment on the possible effects of irradiation on the precipitate structure and composition and on the resulting effects on corrosion.

P. Rudling—We have not investigated irradiated specimens, so we do not want to draw conclusion from that.

N. Ramasubramanian (Chalk River Nuclear Laboratories)—In out-reactor steam tests how does varying the condition of tests from 500°C, 24 h, to 430°C, 30 days, and to 400°C, 200 days, affect the surface appearance of samples?

P. Rudling—There is a gradual change from white nodules dispersed in a black oxide, at 500°C/24 h/10.3 MPa, to grey patches in a black oxide at 400°C/200 days/10.3 MPa.

A. B. Johnson (Battelle Northwest)—(1) In your characterization of oxidation rate differences between Zircaloy-2 and Zircaloy-4, how effectively have you addressed lot-to-lot differences?

(2) We compared steam autoclave oxidation rankings for three Zircaloy-2 lots with rankings for the same lots in-reactor. The rankings in steam at 400, 425 and 435°C were reversed from the ranking in oxygenated irradiated coolant. The rankings for the same lots in low-oxygen coolant gave mixed results, so I do not take exception with your observation of a correlation of PWR cladding oxidation with the 400°C steam test.

P. Rudling—(1) The objective of this work was not to evaluate the lot-to-lot corrosion differences of Zr-2 and Zr-4 cladding lots, and therefore, we do not have the data to address this question.

(2) Beside the corrosion results presented here, we have additional in-pile and out-of-pile corrosion data of cladding tubes from other vendors. These additional data confirm that there exists a correlation between in-pile data, obtained in the Ringhals 3 reactor, and out-of-pile data obtained at 400 and 410°C, but there is no correlation at higher test temperatures.

M. Noe (IAEA)—You correlate corrosion resistance to the size and composition of intermetallics. In another paper it was proposed that corrosion was related to the composition of species dissolved in the matrix rather than to the composition of the intermetallics. What is your opinion on this apparent contradiction?

P. Rudling—The corrosion properties are obviously associated to the intermetallic particle sizes. From this investigation it also seems that a low Fe/Cr ratio in the intermetallics is related to good corrosion properties. However, whether the corrosion properties are a result of the intermetallic particle size and composition, or results from the matrix composition, can not be deduced from this investigation.

A. M. Garde (Combustion Engineering)—Although the range of tin concentration covered in your investigation is small (1.7 to 1.5%), your conclusion of good in-PWR corrosion performance with the higher tin concentration and poor in-PWR corrosion performance with the lower tin concentration appears inconsistent with other investigations.

P. Rudling—The effect of the annealing parameter overrides the effect of the small compositional variations. Since the difference in annealing parameter in the case referred to above is several orders of magnitude, the higher annealing parameter of the material with good corrosion properties, is much more important for the corrosion proposed than the higher tin content of this material.

A. Strasser (S. M. Stoller Corp.)—What effect will the irradiation induced disappearance (resolution?) of intermetallics have on the as-fabricated matrix composition and in-reactor corrosion?

P. Rudling—With the results we have obtained here, it is difficult to speculate on the amount of dissolution, effect on matrix composition, and their in-reactor corrosion behavior.

C. M. Eucken (TWCA)—Do you have additional data showing the beneficial effect of lower Fe/Cr ratio within the intermetallic particles on the PWR corrosion rate? The two distributions shown in the presentation exhibit very little difference.

P. Rudling—The few additional data we have is also in accordance with these observations.

However, it is difficult to unambiguously correlate the particle composition with the corrosion rate.

R. M. Kruger (GE)—What was the relationship between particle size and particle composition?

P. Rudling—The particle size was not recorded together with its composition, so no such correlation could be made.

G. P. Sabol (Westinghouse)—The report of similar hydrogen pickup behavior of Zr-2 and Zr-4 in autoclaves is contrary to many published data. Please comment.

P. Rudling—The data obtained in this project indicate that the hydrogen pickup is about the same for the tested Zr-2 and Zr-4 lots.

R. A. Ploc (AECL)—Is it perhaps the surface finish, rather than the intermetallic particle size which controls the corrosion rate? Different surface finishes produce different geometries that can affect the oxide/metal interface structures, and these structures can be perpetuated throughout the corrosion process. Such structures influence the corrosion rate through oxide cracking. To complete the evaluation of the particular alloy/heat treatment and so forth, a series of tests might be contemplated which includes various surface finishes (to <1 µm finish).

P. Rudling—Out-of-pile corrosion data show higher weight gains for belt ground specimens than for etched specimens. We can not tell from this data whether the surface finish controls the corrosion rate or not.

A. B. Johnson (Battelle Northwest)—Comparisons of in-reactor and steam autoclaving hydride rankings were conducted on three Zircaloy-2 lots in the ETR G-7 loop. In the oxygenated coolant the hydride ranking reversed from the ranking in the steam autoclaves (400, 425. and 435°C). In the hydrogenated G-7 loop coolant, the results were mixed. How strong is the evidence that there is a correlation for oxidation between 400°C autoclaving and in-reactor PWR environments?

T. Thorvaldsson—Further results after two cycles confirms the correlation.

Development of a Cladding Alloy for High Burnup—GEORGE P. SABOL, GERALD R. KILP, MALCOLM G. BALFOUR, AND ELWYN ROBERTS, pp. 227–244.

Dr. B. D. Warr (Ontario Hydro)—(1) You have observed accelerating corrosion for Zr-2.5Nb out-reactor only when the lithium content is increased during the test. Is this correct?

(2) During your in-reactor tests you observed accelerating corrosion in Zr-2.5Nb after approximately 50 GWD. Was this associated with a change in environment in-reactor? Do you believe these results are reproducible? After over 100 000 EFPH exposure in CANDU reactors, Zr-2.5Nb has not shown this type of behavior.

G. P. Sabol—(1) We observed out-of-pile accelerated corrosion with the 2.5 Nb alloy only in lithiated water containing 35, 70, and 700 ppm lithium. In water containing 3.5-ppm lithium, no breakaway corrosion was observed for exposure up to 112 days, the maximum time tested at this concentration.

(2) We cannot identify any unique reactor parameter that changed when the Zr-Nb rods reached burnups of 50 to 60 GWD/MTW. However, there was a large increase of crud deposition in the fuel rods, beginning with Cycle 4A (2nd cycle for *W* rods).

We do not know if the deleterious corrosion performance of the Zr-Nb binary alloys is reproducible.

E. G. Price (AECL)—Was the hydrogen pick-up after the BR-3 tests measured? Was the hydrogen pickup in proportion to the oxide thickness/weight gain?

G. P. Sabol—Hydrogen pickup was measured as part of the post-irradiation examination of the BR-3 rods. The percent theoretical hydrogen pickup was approximately 11% for both ZIRLO and Zircaloy-4. The absolute hydrogen pickup of ZIRLO was less than that of Zircaloy-4 because of its superior corrosion performance.

H. G. Weidinger (Siemens)—Could you please give the cladding temperatures at the peak oxidation positions of the fuel rods where you compared Zry-4 and alloy-E?

G. P. Sabol—Assuming minimal crud deposition, the time-average cladding metal/oxide interface temperatures at the peak corrosion region above the middle grid for the Zircaloy-4 rod in the top of Fig. 9 were 578, 599, and 583 K, for Cycles 3B, 4A, and 4B, respectively; maximum temperatures within each cycle were 591, 620, and 603 K, respectively, as calculated by the Westinghouse PAD design code. The corresponding temperatures for the other rods in Fig. 9 are similar, as the rods have been matched for power histories. However, the actual temperatures in Cycles 4A and 4B were probably somewhat higher because of thick crud deposits that formed on the BR-3 rods during this period.

Dr. J. E. Harbottle (CEGB)—(1) What was the reduction ratio of the ZIRLO tubing and was the texture similar to that of normal Zr-4 cladding?

(2) Have you measured the ISCC behavior of ZIRLO?

(3) Do you have any power ramping experience of ZIRLO clad rods?

G. Sabol—(1) The reduction in the first cold pilger step was approximately 50%. The reductions used in the remaining four pilger steps ranged from 60 to 62%.

The processing sequence resulted in a splitting of the basal poles, similar to that of typical Zircaloy-4 tubing. Furthermore, the contractile strain ratio of ZIRLO tubing was very similar to that of 15×15 Zircaloy-4 tubing.

(2) The ISCC behavior as measured by both SIMFEX tests in iodine and by internal pressurization in $(Ar + I_2)$ is similar for ZIRLO and Zircaloy-4.

(3) No. We have no power ramping data to report.

H. M. Chung (Argonne National Laboratory)—Irradiation-induced or enhanced phenomena (such as irradiation-induced segregation, precipitation, and hardening-embrittlement) are generally known to be sensitive to temperature and dose rate. In that respect, the somewhat lower (approximately 70°C) temperature of the BR-3 reactor may produce quite different results of mechanical properties from PWR conditions. Some reported data on radiation-anneal hardening and strain aging showed indeed significantly different responses for approximately 250°C and approximately 320°C. Could you kindly comment on this effect?

G. P. Sabol—Your value of 70 K difference is too high. The difference in average outlet temperature between a commercial PWR and BR-3 is more like 45 K. Regardless, the post irradiation mechanical behavior of the ZIRLO alloy was not determined. However, high burnup Zircaloy-4 rods exposed in equivalent positions to the ZIRLO rods in BR-3 were subjected to burst testing at 616 K. These results (reported in DOE/ET 34073-1, Nov. 1982) indicate that the values for clad ductility and failure stress of the BR-3 rods were comparable to those of rods taken from the Zorita commercial PWR.

Enhanced Low-Temperature Oxidation of Zirconium Alloys Under Irradiation—BRIAN COX
AND V. FIDLERIS, pp. 245–265.

A. B. Johnson Jr. (Battelle Northwest)—(1) How do the low-temperature kinetics fit on extrapolations of kinetics from higher temperatures?

(2) In examination of G-7 loop specimens, polarized light was an effective method to identify zones of porosity in the oxides. Does the porosity in the thin films respond to polarized light techniques?

B. Cox—(1) Very well. The ATR results fit right on the extrapolated curves presented by me at the 2nd International Symposium on Degradation of Reactor Materials, Monterey, 1985 (Ref 2 of text), when allowance is made for the high flux in ATR, and assuming the irradiation enhancement is additive and athermal.

(2) Yes. The grey appearance shown clearly in dark field optical micrographs shows up even more clearly with polarized light techniques.

B. Cheng (GE)—The low-temperature oxidation you described in the paper had a thickness range of ≈1000 to 5000 Å. What is the size range of the precipitates in the samples? Could the precipitates play a role in the anodic dissolution and pore formation process?

B. Cox—It was thought initially that precipitate size and frequency would be an important factor in this study, hence the selection of a range of grades of zirconium as well as Zircaloy-2 and Zr-2.5Nb. In practice the effect of the UV irradiation largely swamped any differences in the material batches. It might be expected that a less severe test would allow some of these effects (such as precipitate size) to reveal themselves, but no such effects were observed. The Zircaloy-2 was a well annealed batch of sheet with precipitates in the range 0.1–0.6 μm with a small tail of larger precipitates in the distribution. Two of the three grades of zirconium also contained distributions of Zr/Fe precipitates.

Nodular Corrosion

A Systematic Survey of the Factors Affecting Zircaloy Nodular Corrosion—KEIZO OGATA, MISHIMA YOSHITSUGU, TADATSUNE OKUBO, TOSHIMASA AOKI, TAKUYA HATTORI, TORU FUJIBAYASHI, MASAHISA INAGAKI, KAZUO MUROTA, TATSURO KODAMA, AND KATSUHIRO ABE, pp. 291–314.

N. Ramasubramanian (AECL)—Is a two step out-reactor nodular corrosion test better than a single step corrosion at 500°C, 10.3-MPa steam to predict in-reactor behavior?

K. Ogata—Both one-step and two-step tests in 10.3-MPa steam showed similar results in the degree of nodular corrosion. I think however, the two-step test is better from the viewpoint of reproducibility.

L. Van Swam (ANF)—(1) Was the tubing on which the tests were carried out in the stress relieved or recrystallized condition?

(2) Was there any effect of grain size on the nodular corrosion susceptibility? It seemed that the material with the highest degree of final cold work had the best nodular corrosion resistance. Could you comment on this?

K. Ogata—(1) All tubes tested were in the recrystallized condition.

(2) Grain size was not measured in this study, but data from tube manufacturing and inspection showed a consistent grain size for almost all specimens in the range of 12 to 13 in ASTM No. Final cold working may be a possible factor affecting nodular corrosion, but its relation with the corrosion was not clear in this study.

H. Klepfer (Exec. Tech. Inc.)—In reactor you saw extensive nodular corrosion. Was this a commercial BWR? Was it one with relatively high copper content in the reactor water? Did you see any CILC fuel rod failures?

K. Ogata—Fuel rods shown in this presentation were irradiated in a Japanese commercial BWR. Its water chemistry is well controlled with low copper content. We have no fuel failures induced by CILC.

G. P. Sabol (Westinghouse)—(1) Did you attempt to correlate the susceptibility for nodules in the autoclave tests with the thermal anneal parameter A?

(2) Did you try a regression analysis or Expert System system analysis of the data to identify a correlation between properties and nodule susceptibility in the autoclave test?

K. Ogata—(1) No. We have not calculated the annealing parameter A.

(2) Tests were conducted using existing cladding tubes and fabrication parameters varied across a wide range. However, kinds of specimens were not enough to make a statistical analysis.

B. Cheng (GE)—Your data show that nodular corrosion does not form at temperatures below 490°C. This is consistent with my experience on more recent Zircaloy. Several papers earlier in this symposium have indicated that they can produce nodular corrosion at temperatures in the 400 to 450°C range. What is your experience? Have you ever seen nodular corrosion in autoclave tests at temperatures below 480°C?

K. Ogata—No, we have not produced nodular corrosion on Zircaloy-2 by steam tests at temperatures below 480°C.

Corrosion Performance Ranking of Zircaloy-2 BWR Applications—PETER RUDLING AND A. J. MACHIELS, pp. 315–333.

H. G. Weidinger (Siemens)—From your first slide, I cannot conclude which material treatments were used, besides one variant which was beta quenched. Was there (alpha + beta) quenched material included in this progress?

P. Rudling—The four different cladding types, designed by II to V, were subjected to different thermomechanical treatments, specifically the intermediate heat-treatment temperatures and fines were varied between the different cladding types. Only one of these cladding types, namely, Type III cladding, was beta quenched at an intermediate stage, while the other three types were heat-treated in the alpha-range.

B. Cheng (GE)—(1) What is your prefilming condition? How do you compare your sample prefilming procedure to the two-step corrosion test proposed by GE in the last zirconium meeting held at Strasbourg, France?

(2) You showed the effect of O_2 and H_2 on the corrosion weight gain. It appears that the weight gain changes are not very much. Do O_2 and H_2 influence the nodular corrosion susceptibility significantly?

P. Rudling—(1) Our prefilming procedure is similar to GEs and is carried out at about 425°C for 6 h and leads to a black oxide thickness of 0.5 to 1.0 μm.

(2) The O_2 and H_2 additions to the steam do not have a large impact on the corrosion performance on corrosion resistance cladding, such as Type III cladding. However, these additions have a large impact on the corrosion performance on noncorrosion resistant cladding, such as Type IV cladding, and consequently have a crucial impact on the nodular corrosion susceptibility of this cladding type (Type IV).

R. B. Adamson (GE)—Your results seem to be in line with those presented by GE at the Strasbourg meeting. Do you think that a 510°C temperature would be equivalent to your proposed 520°C temperature?

P. Rudling—If the temperature variation within the autoclave is below about ±1 to 2°C, a discriminating test can be carried out at this nominal temperature. However, since most standard autoclaves show internal temperature variations between the different fixture positions (where the samples are hung) in the range of 6 to 15°C, we believe that the nominal temperature has to be raised to at least 520°C. This is to ensure that the lowest temperature in the autoclave is sufficiently high (to be discriminating).

Influence of Chemical Composition and Manufacturing Variables on Autoclave Corrosion of the Zircaloys—RONALD A. GRAHAM, JACK P. TOSDALE, AND PETER T. FINDEN, pp. 334–345.

J. F. Bates (Western Zirconium)—(1) Could you comment on any correlation of corrosion with interstitial (carbon, oxygen, nitrogen and hydrogen) contents? Also, what were the concentration of these elements?

(2) Since the variations used were from a production ingot, and hence represent normal production variation, what would you do to obtain an entire ingot with composition at the "point of indifference"?

R. Graham—(1) The second melt electrodes that made up the final melt ingot were intentionally made from the same sponge blend in order to keep the interstitials at a constant level. Oxygen was about 1200 to 1300 ppm, carbon = 160 ppm, nitrogen = 30 ppm, and hydrogen < 10 ppm.

(2) The iron, chromium, nickel, and tin levels were intentionally varied by the design of the final melt electrode, and therefore are not representative of normal production variations. The bottom half of the 5500-kg electrode was made of "controlled composition" with low tin and high iron, chromium, and nickel as shown by Table 1. Current manufacturing practices permit 680-mm by 8000-kg ingots to be melted routinely within the controlled composition portion of the ASTM Zircaloy-2 specification range.

B. F. Kammenzind (Westinghouse)—We have seen two papers now that suggest decreasing the tin content improves the corrosion resistance of zirconium alloys as determined by weight gain in a 500°C steam test. Do you know whether the improvement is due to a decrease in either the number density or size of nodules developed is it due to a decrease in the thickness of the uniform film formed away from the nodular regions.

R. Graham—We did not form nodules on any of the coupons tested. We used the uniform weight gains as a measure of the sensitivity towards nodular formation. Thus, in this case decreasing the tin content reduced the thickness of the uniform film. We do not have evidence of the effect of tin on nodule morphology, size, or number density.

C. D. Williams (GE)—The plot of weight gain versus cooling rate showed a scale of cooling rate moving to approximately 300°C/s. Did you characterize the precipitate size distribution in alloys quenched near this cooling rate?

R. A. Graham—We have performed a limited analysis of precipitate number frequency. Increasing cooling rates leads to increased supercooling which activates additional nucleation sites. The corrosion weight gains decrease with increasing number density of precipitates.

Initial results correspond closely with data presented by Cheng and Adamson (Seventh International Conference on Zirconium in the Nuclear Industry, Strasbourg, France). Our fastest cooled sample was only 293°C/s, and we do not have data at cooling rates of 1000°C/s where one would expect martensite (precipitate free) to form.

Effects of Alloying Element Distribution on the Nodular Corrosion of Zircaloy-2—KEIZO OGATA, pp. 346–359.

B. Cox (AECL)—Were the tin, iron, nickel, and chromium analyses on the sample showing the sharp discontinuity in nodular oxide coverage made on the surface after oxidation or not?

K. Ogata—Specimen for the analysis was taken from the tube axial location next to the corrosion test specimen. Therefore the analysis was made on the surface without oxidation.

E. F. Baroch (Consultant)—What were the conditions for the alpha plus beta heat treatment, and the quench conditions?

K. Ogata—The specimen alpha plus beta quenched at the final tube size was held at 900°C for 2 min and water quenched.

A. B. Johnson (Battelle Northwest)—I previously proposed an alloy depletion hypothesis (EPRI NP-5132) for nucleation of nodular corrosion. A key aspect of the concept is that depleted zones serve as nodule initiation sites. Once the oxidation begins to penetrate into the base metal, it becomes self-propagating because of stresses caused by the larger volume of the oxide compared to the corresponding metal volume. Do you agree with that concept?

K. Ogata—I agree. Alloy depleted areas can be oxidized faster than surrounding normal area. This can cause oxide cracks that lead to nodular corrosion.

R. M. Kruger (GE)—(1) What was the surface treatment used on the samples before the microprobe analysis?

(2) Given the large size of the area analyzed, as well as the depth that the X-ray signal comes from, do these results indicate a long-scale variation in solute concentration, or is this variation attributable to individual precipitates?

(3) Could this technique be recommended as a quality control tool?

K. Ogata—(1) The specimen surface for the analysis was mechanically polished but no chemical treatment was done on it.

(2) The analyzer detects signals from both solutes and precipitates existing in the given area within a depth of several microns. Therefore, this method cannot distinguish whether the variation in nodular corrosion susceptibility can be attributed to the solutes or to the precipitates.

(3) Measurements of alloying element distribution can be a tool for quality control but further verification should be made using in-pile data.

C. M. Eucken (TWCA)—(1) Our experience with electron microprobe analysis shows that for beam size of about 2 μm diameter the variation in iron, chromium, and nickel is merely a statistical probability of hitting (or missing) a large particle on the surface of the sample. Can this explain the variations shown in your work?

(2) Likewise, our experience shows that iron, chromium, and nickel variations existing in the as-cast ingot can be rehomogenized in a matter of 1- or 2-min holding time in the all-

beta region. Differences in concentration after beta quenching are due to reprecipitation. What is your comment?

K. Ogata—(1) Measuring spot size in this study was 10 μm square, which covers an area of several grains of Zr-2. The statistical evaluation of a total of 250 000 data can represent a distribution of the total amounts of each alloying element within the measured area. This includes both a statistical probability of hitting or missing a large precipitate and a probability of a large or small number density of precipitates. Effect of solute element can also be included, but it is presumed to be small because of low solubility.

(2) The homogenization effect of beta quenching may be caused through redissolution and reprecipitation processes during the quenching. The distribution could be varied by the cooling rate that affects the size of both precipitates and alpha-Zr platelets.

H. M. Chung (Argonne National Laboratory)—Your observation within a single tube section of two side by side bands, one with heavily developed nodules and the other free of the nodular oxidation, is quite striking. Are the chemical compositions of the materials of the two bands drastically different? One would assume that the thermomechanical process, and hence, the accumulated annealing parameter, within the single tube section would be practically the same.

K. Ogata—One lot of specimens showed a clearly different degree of nodular corrosion within a single tube surface. A clear boundary was seen between areas with large and small numbers of oxide nodules, and it continued along the tube axis.

The difference in nodular corrosion coincided well with the regional difference in contents of alloying elements tin, iron, chromium, and nickel which were analyzed by the CMA analyses on the area including the boundary. A region of heavy nodules contained about 10% smaller amounts of these elements than the other. This difference in chemical composition can be a cause for the discontinuity in the degree of nodular corrosion.

Electron Microscopy Study of Oxide Films Formed on Zircaloy-2 in Superheated Steam— BANG-XIN ZHOU, pp. 360–373.

A. M. Garde (Combustion Engineering)—(1) For the calculation of the stress gradient in the curled oxide, is the elastic analysis appropriate or is an elastic-plastic analysis necessary? Is the plasticity caused by remaining substrate metal?

(2) On the basis of the model for nodular corrosion of Zircaloy that you are proposing can you explain: (a) the ease of getting nodular corrosion in a 500°C but not in a 400°C steam test and (b) suppression of nodular corrosion in beta quenched material?

Zhou Bang-xin—(1) At high temperature (673 to 773 K) the black oxide film could be deformed plastically under compressive stress, but it depends on the level of stress. Now the curled oxide film formed at room temperature, since the metal was dissolved after autoclaving. So I think that the elastic analysis for the calculation of stress gradient is appropriate.

The plasticity of black oxide film means that the film itself may be deformed plastically when the stress reaches a certain level at certain temperature.

(2) The model that I have proposed for the nodular corrosion can be divided into three stages. The first stage is epitaxial oxide film formed on the surface in different thickness from area to area. The second stage is the formation and development of bumps in the

black oxide film. The third stage is the formation of white nodules after the diffusion and condensation of vacancies in the bumps. All three of these stages are closely related to temperature. If temperature is lower, the epitaxial oxide film grows slowly; the metal matrix becomes stronger and less easy to deform, which is necessary for the formation and development of bumps according to this model. At low temperature the diffusion of vacancies in bumps becomes difficult, even if the bumps could form. So it is easy to get nodular corrosion in a 773 K but not in 673 K steam test. If the temperature and time at which the autoclaving is carried out is plotted with the nodular corrosion behavior, a map that might be similar to the N-S diagram for fatigue may be obtained according to this model. The temperature 773 K might be at the position indicated by the arrow. The curve, which is the boundary between nodular corrosion and uniform corrosion, could be also shifted due to the change of microstructure, alloy composition, or the environment conditions.

Beta quenching will change the size and distribution of second phase particles in samples, and bring a supersaturation of alloy elements in solid solution in the matrix. These will affect the surface energy of crystals with different orientations. If the thickness difference of epitaxial oxide film is less, then it is difficult to form bumps. On the other hand, if the growth rate of oxide film decreases because of the change of structure and the composition of matrix after beta quenching, this will also retard the formation of bumps.

We have investigated the nodular corrosion behavior in the heat affected zone of electron beam welded samples. The heat affected zone has very good nodular corrosion resistance. There is a sharp boundary between black oxide film, which is on the heat affected zone, and white oxide film. When the microstructure of the heat affected zone is examined, the results show that the equiaxed grains near the black/white oxide boundary also possess good resistance to nodular corrosion. This means that the supersaturation of alloy elements in solid solution also play an important role in suppression of the nodular corrosion.

We are planning to make a vertical section of thin specimens for TEM examination. Then it might be possible to examine the structure of oxide film at different depths, and the oxide/metal interface where the oxide just forms. Then we could get more information to know how and why these factors affect the oxidation process.

Heterogeneous Scale Growth During Steam Corrosion of Zircaloy-4 and 500°C—DANIEL CHARQUET, ROLAND TRICOT, AND JEAN-FRANCOIS WADIER, pp. 374–391.

Dr. B. D. Warr (Ontario Hydro Research)—What was the surface preparation of the specimens for corrosion testing?

D. Charquet—The specimens have been pickled before steam exposure.

B. Cox (AECL)—It seems to me that many of the materials you report on were heat treated so that they would fail the normal 400°C steam acceptance test which all materials going into reactor must pass. I would like you to comment therefore on the relevance of your observations to materials that have passed the 400°C test. The effects of "poor" heat treatment resulting in "stringer corrosion" and attack on "depleted" grains after alpha plus beta treatments have been known for many years. Can you be confident that observations made on such materials will be comparable to effects of the same variables on cladding material such as that showing nodular corrosion in BWRs?

D. Charquet—Materials for BWR have a grain size so small that it makes difficult the observations of the early stage of the nodular corrosion. The purpose of this study was to

prepare "model samples" with a grain size large enough to show the different effects of orientation and intermetallic distribution. We think that the factors evidenced in this study are relevant for the understanding of the nodular corrosion of BWR materials.

Obviously some structure like the alpha plus beta one does not pass the 400°C as well as the 500°C tests, but it was not the intent of this study to prepare corrosion resistant materials.

B. Cheng (GE)—You showed higher oxide growth rate along acicular, precipitate-free grains and the absence of the corrosion of adjacent grains. Is this caused by the orientation effect or the solute depletion effect? Both situations may be produced by the specific heat treatment you gave to your specimen. Do you have any microanalysis studies to determine whether there is local chemistry variation?

D. Charquet—The larger oxide layer on a particular grain of Picture 2 is due to a favorable crystallographic orientation since the neighboring needles have different colors under polarized light.

The iron or chromium content in the matrix is too low to be measured by electron microprobe. Only the atom probe could be of some help to determine so low a concentration in the solid solution.

H. M. Chung (Argonne National Laboratory)—Some of your microstructure shows secondary (breakaway) recrystallization. What were the conditions for the secondary recrystallization? What was the crystal orientation of maximum growth?

D. Charquet—Coarse equiaxed grains were not observed after primary recrystallization, but they were produced by critical strain and annealing. We do not know the relationship existing between crystal orientation and growth rate at 500°C under 10.3 MPa.

Automatic System for Measuring the Zirconium Liner and Zircaloy-2 Thickness of Zirconium Liner Tubes—MASAHIRO HONJI, TAKAHIDE SAKAMOTO, YOSHIFUMI MORIMOTO, AND SHIGETOSHI HYODO, pp. 392–404.

C. A. Williams (GE)—How many records does the inspection require for a full length BWR fuel tube?

M. Honji—The automatic measurement of a tube takes 2 min.

J. Schemel (SSM)—How long does a coil probe last in the inspection process?

M. Honji—A probe lasts for about one month.

H. Rosenbaum (GE)—I compliment the authors and Sumitomo Metals for accomplishing a difficult task so well. In your paper you considered the effect of tin on the resistivity and its effect on the thickness measurement. Would you please comment on the effect of iron, nickel, chromium, and oxygen?

M. Honji—We have investigated the effect of iron, nickel, chromium, and oxygen. The output of the measurement is hardly affected by these factors. These factors can be ignored if these are controlled within the ASTM specification.

H. D. Sharma (Nuclear Power Corporation, Bombay)—Can this technique be used to measure the thickness of cadmium and zirconium sandwiched structure or cadmium sandwiched to Zircaloy-2?

M. Honji—Yes, it is possible to measure the cadmium and 304 L stainless steel thicknesses, and cadmium and Zircaloy-2 thicknesses by this technique.

P. Dunstan (SSM)—Does the eddy current method of measuring liner thickness give an *average* thickness value at a particular cross section, or does it give an absolute value that reflects the maximum or minimum liner thickness at one cross section?

M. Honji—It gives an average thickness. The measuring width of the eddy current method is around 0.8 mm because the diameter of the coil is 0.8 mm diameter.

Basic Metallurgy

Solubility Limits and Formation of Intermetallic Precipitates in ZrSnFeCr Alloys—DANIEL CHARQUET, ROLAND HAHN, ERHARD ORTLIEB, JEAN-PIERRE GROS, AND JEAN-FRANCOIS WADIER, pp. 405–422.

H. S. Rosenbaum (GE)—Is there an effect of precipitate size (at the smallest sizes) on the apparent solubility or matrix concentration of iron and chromium?

E. Ortlieb—Our results of the measurement of the thermoelectric power of beta-quenched and subsequently annealed Zry-4 specimen suggest that the average solute content remains constant after the precipitation process is finished. We conclude that the average solute content does not change during the ripening process of the precipitates and thus does not depend on the size of the precipitates. However, the study of the growth mechanism shows that concentration gradients should exist in the vicinity of the surface of individual particles, which act as a driving force for particle growth.

R. M. Kruger (GE)—(1) In the size distributions shown, were there one or two types of precipitates?

(2) How do these results compare with literature data, for example Stupel et al. [3] on similar systems? Does the presence of tin make a difference?

E. Ortlieb—(1) The specimens investigated for their precipitate size distribution exhibited an Fe/Cr-ratio of about 2. According to our results on the influence of the Fe/Cr-ratio in the alloy on the nature of precipitates formed, only $Zr(Fe,Cr)_2$-particles would be expected for a ratio of 2.

(2) Recent data obtained by Mossbauer Spectroscopy [3] show a solubility of iron in alpha-Zr close to the results of our study. With regard to chromium however, the solubility limit in alpha-Zr reported in the literature [4] is considerably higher as compared with the solubility found for a Zr1.4%Sn0.1%O-matrix.

G. Hood (AECL)—(1) The equilibrium solid solution content of iron in alpha-Zr at 700°C is established instantaneously. I would guess the free iron atom jump frequency is approximately $10^{10}s^{-1}$ at 700°C minus the temperature of your growth kinetic studies.

According to theory, the Ostwald ripening process should reach an effective equilibrium when all of the particles have reached a common size. Do you see any sign of an approach to this?

E. Ortlieb—We did not observe indications of a saturation of the particle growth process in the range of annealing temperatures and annealing times applied to our specimens.

H. M. Chung (Argonne National Labs)—Is your activation energy of precipitate growth consistent with the activation energy of the accumulated annealing parameter (ΣA) that was presented in Session III by Garzarolli et al., that is, approximately 80 kcal/mole?

E. Ortlieb—The data currently available from this study are still not sufficient to determine a sound value of the activation energy of precipitate growth. More specimens have to be analyzed that have been annealed at different temperatures and for different times in the alpha-phase range.

Direct Measurement of Matrix Composition in Zircaloy-4 by Atom Probe Microanalysis—
BOEL WADMAN AND HANS-OLOF ANDREN, pp. 423–434.

G. M. Hood (AECL)—You report on differences in properties of Materials A and B in terms of corrosion properties and apparent iron solid solubility as functions of heat treatment. You also consider that the iron in solid solution may reflect on equilibrium distribution formed by bulk iron diffusion in the matrix. In terms of the temperatures and time scales, the equilibrium concentration of iron in solid solution would be established "more or less instantaneously" [5] while the amount of Fe in "genuine solid solution" would literally be <60 ppm atomic [6] and not 160 to 640 ppm as in your experiment.

It is highly probable, then, that the time scales of the annealing treatments have resulted in the development of "structures" associated with a slowly diffusing substitutional component such as tin. It is known from positron annihilation spectroscopy (PAS) work [7] that Sn atoms in Zircaloy & Zr-1.08 wt%Sn tend to form submicroscopic clusters, while TEM studies [8] of irradiated Zircaloy-2 and Zircaloy-4 show that iron tends to associate with tin in these alloys. Therefore, I suggest that in your experiments the heat treatments are developing submicroscopic complexes with [Zr/Sn/Fe. . .] such that the iron is made to appear to be in solid solution-unless it really is in a complexed form. In addition, the "clustering of the tin atoms" in these complexes might well be responsible for the improved corrosion resistance of Material A.

B. Wadman—The hypothesis of complex formation or clustering in Zr-4, involving tin and possibly iron is very interesting. It might be possible to detect such structures by atom probe analysis.

Although the order of arrival of ions at the ion detector does not reflect the exact arrangement of atoms in the analyzed volume, it is often also possible to detect very small clusters by statistical treatment of atom-probe data. We shall examine this possibility.

G. P. Sabol (Westinghouse)—I am most impressed with this new experimental data, but the previous paper indicates a solubility limit of iron below that find of 0.04%. Also, their thermoelectric rate data indicate relatively rapid attainment of equilibrium in the matrix. Can you rationalize your data with that of the previous paper?

H. O. Andren—The measured iron concentration in the matrix of Material A is higher than the equilibrium concentration measured by Charquet et al. in a Zr-4 type alloy. If our measurement represents an equilibrium concentration, the impurity content in commercial Zircaloy-4 must affect the iron activity considerably. Another explanation could be that for some reason we do not attain the equilibrium concentration of iron in spite of the 3.5-h final annealing. However, this is in apparent contradiction to the kinetic data for Zircaloy-4 measured by the same authors.

B. F. Kammenzind (Westinghouse Bettis)—(1) Could you elaborate on your procedure to field evaporate the oxide layer formed during electropolishing.

(2) Do you have any suggestions for improving specimen reliability, that is for obtaining more than ten useful specimens out of 26 prepared.

B. Wadman—(1) The anodic oxide layer is field evaporated away at a specimen temperature of 90 K. The evaporation process is monitored by neon field ion microscopy.

(2) According to our experience, factors of importance for the ability of a Zr-4 specimen to support the mechanical stress are as follows:

- anodic oxide layer thickness
- surface smoothness
- geometry (tip radius and cone angle)

The oxide layer can probably be reduced by electropolishing at a lower voltage. This requires an electrolyte, which gives a smooth specimen surface at lower polishing voltages.

It is also important to minimize the volume at high mechanical stress, by using specimens with a small tip radius and a not too small cone angle.

R. B. Adamson (GE)—Can you comment on the statistical significance of the values of iron and chromium that you report? If my calculation is correct, the total number of iron ions observed in your experiment is about 5, which seems to be quite small to someone not familiar with the technique.

B. Wadman—Because of the low noise level (high signal-to-noise ratio) and the high mass resolution (FWHM <1/500) all signals at correct mass-to-charge ratios are considered significant.

The statistical accuracy is approximately given by the standard deviation of the binomial distribution. For a small number of ions N this is simply $\sqrt{N}$.

H. H. Klepfer—It is interesting to note that the matrix iron and chromium contents you report for the alloy with the best corrosion performance were higher than the solubility limits for iron and chromium reported in this conference by Charquet et al. For the poor performing material; you report iron and chromium near the limits of solubility reported by those authors. Heat treatment effects are suggested in your paper as being responsible for both the differences in matrix composition and corrosion differences. Yet in another paper in this conference Graham et al. report insensitivity of corrosion performance as nickel content is increased in the Zircaloys. Might it not be that nickel solubility and concentration in the Zircaloy matrix is a very important determinant of Zircaloy corrosion performance?

Neither your paper nor that of Charquet et al. report work on nickel. Do you plan work on Zircaloy-2 or other nickel containing alloys?

H. O. Andren—So far our work has been concentrated on Zircaloy-4, in which the nickel content is below the detection limit of atom probe analysis. However, analysis of Zircaloy-2 is included in our research program.

H. M. Chung (Argonne National Labs)—You have shown ZrO^{2+} and ZrO^{3+} complexes detected in your atom probe signals. Where are the complexes coming from, that is, are they from the matrix?

B. Wadman—Molecular ions such as ZrO^{2+} and ZrO^{3+} are formed by atoms that were nearest neighbors in the matrix and have field evaporated together. This phenomenon is frequently observed during atom probe analysis of oxygen-containing materials.

Diffusion of 3D Transition Elements in α-Zr and Zirconium Alloys—GAVIN M. HOOD AND RAYMOND J. SCHULTZ, pp. 435–450.

R. A. Holt (Ontario Hydro)—Are the distances involved in sweating of iron from the Zr-0.1%Fe crystal consistent with the diffusion coefficient measured for iron in alpha-Zr?

G. M. Hood—In terms of the work that we have done to date the reprecipitation phenomenon does seem to take place on a time scale that is consistent with our data for iron spacer diffusion in alpha-Zr.

M. Leger (Ontario Hydro)—Have you noted any iron concentration dependence of the low-temperature diffusion coefficient measured with your tracer technique? In a situation in which the iron is forming complexes, one might expect effects on the measured tracer diffusion coefficient because of the presence of other isotopes of iron.

G. M. Hood—In our measurements the tracer ^{59}Fe concentration is trivial compared to the residual iron in the specimens (either as an impurity or present deliberately as in ZrFe alloy). I do not recall seeing an effect, such as you mention, probably because the "Fe concentration is relatively uniform" across the specimen. However, I cannot give an unequivocal reply to your question: possibly some comments I have made in our paper for the proceedings would be useful. As we have seen at this meeting iron in zirconium is a very complicated subject!

T. Thorvaldsson (AB Sandvik Steel)—In commercial alloys we have very small grain sizes, and the important heat treatments are performed at low temperatures where one normally would expect grain boundary diffusion. Can you compare, or comment, on differences between fast intrinsic diffusion and grain boundary diffusion rates?

G. M. Hood—It seems not uncommon to find that dislocation and/or grain boundary diffusion is faster than bulk diffusion even for the very fast interstitial diffusers. We do not see any overt signal of grain boundary effects in our alloy data, but the question is there and is addressed in the text of our paper. It is also tackled in a review I have written on diffusion in alpha-Zr to be published (this year) in The Journal of Nuclear Materials.

B. Cox (AECL)—Do you find that iron segregates as efficiently to grain boundaries in zirconium as it apparently does to a free surface?

G. M. Hood—We have not studied this aspect "per se," but we have seen very strong decoration of an "included grain" around its boundary surface in an otherwise single crystal specimen. The micrograph suggests an added attraction for iron precipitation at the grain boundary surface. Whether the strong decoration continues down the boundary into the bulk of the specimen is not yet known. Bob Ploc sees very strong preferred (ZrFe) precipitation at grain boundaries in his Zr-0.5 wt% Fe alloy, as described in this conference, but how it might relate to the free surface would be a question for Bob.

Prof. K. L. Murty (North Carolina State University)—(1) Do you know of any measurement on the anisotropy of self-diffusion in Zr? What is the anisotropy of D_{SD}, and do you have data on the activation energies for self diffusion parallel and perpendicular to the basal plane.

(2) Does the anisotropy in diffusion arise from differences in Q_{SD} or D_o?

(3) Since you studied iron diffusion in a large range of temperatures, you do not expect to see a transition in the Arrhenius plot (in D versus $1/T$) because of matrix versus grain boundary diffusion?

G. M. Hood—(1) The only data I know of for $D_\parallel$ and $D_\perp$ for self diffusion is in our 1974 *Acta Met Paper*, $D_\parallel \sim 1.1 \times D_\perp$? In general the differences in activation energy for $D_\parallel$ and $D_\perp$ are so small that it is not clear whether the anisotropy for fast diffusors $D_\parallel/D_\perp \sim 4$ comes for h^D or D_o. ^{51}Cr is an exception: here h^D perpendicular $> h^D$ parallel. The data for high temperature (Fe) + (Ni) in alpha-Zr have too much scatter to say precisely whether h^D parallel $\neq h^D$ perpendicular. We have not seen grain boundary diffusion effects in any obvious way, but the question is tackled in the paper.

J. Harbottle (CEGB)—Could I invite you to comment on the relative merits of nickel and tin in providing corrosion resistance to Zircaloy? Dr. Klepfer has suggested that nickel may stabilize the microstructure, but you have shown that the nickel atom is a rapid diffuser. Are these two observations mutually compatible?

G. Hood—I am not familiar with the sensitivity of the corrosion properties of Zircaloys to their chemical composition. I can say, however, that nickel in pure zirconium is, intrinsically, an ultra-fast diffusor ($D \sim 0^{-10}$ m²s⁻¹ at 800°C); but in both Zircaloy-2 and Zr-2.5 wt% Nb, nickel diffusion is strongly attenuated, presumably by interaction with alloying elements. It is not beyond reason to suppose that nickel, in the form of some strongly bound complex, might have some stabilizing influence on the microstructure; in this general area of discussion, one might note that tin in lead has a remarkably strong interaction with nickel, reducing the diffusivity of the latter (in lead) by orders of magnitude at low temperatures. Nickel in lead is also an ultra-fast, interstitial diffusion.

Intermetallic Precipitates in Zirconium-Niobium Alloys—XIANYING MENG AND DEREK O. NORTHWOOD, pp. 478–486.

E. F. Baroch (Consultant)—You show in your figures no evidence of niobium substituting for niobium in the iron- and/or chromium-containing precipitates. Is this a correct interpretation?

D. Northwood—This is correct. EDS spectra of extracted particles showed no evidence of niobium peaks.

Magnetic Study of Zircaloy—CHIE MIYAKE AND TOSHITO TAKAMIYA, pp. 487–497.

N. Ramasubramanian (AECL)—(1) Have you done measurements on hydrided Zircaloy-4?

(2) Hydrogen uptake by Zr-Fe-Cr precipitates would have effect on magnetic susceptibility. Please comment.

C. Miyake—(1) I have not yet done them. (2) Yes, it would have an effect on their magnetic susceptibility.

B. Cheng (GE)—Have you performed, or will you in the future perform microscopic studies using high-resolution electronic microscopes to confirm whether there are fine Zr-(FeCr)₂ precipitates in the range of 10 to 15 Å in the beta-quenched Zircaloy-4 you discussed?

C. Miyake—I am sorry I have no facility to make such observations at hand.

B. Cox (AECL)—Can you be sure that the small particles that you see by your magnetic technique are present in the beta-phase as you claim? Is it not more probable that the small particles form during the quench?

C. Miyake—I am not sure whether small particles exist actually in beta-phase at high temperature above 900°C or they appear during quenching and/or annealing.

Figure 6 in the paper, which shows the behavior of magnetization after annealing, may partly answer your questions.

Oxidation Kinetics and Auger Microprobe Analysis of Some Oxidized Zirconium Alloys—
ROBERT A. PLOC, pp. 498–514.

B. F. Kammenzind (Westinghouse Bettis)—In the case of the unalloyed zirconium, where you were surprised to see breakaway corrosion occur in dry oxygen, were the regions of deep oxide penetration located at precipitate sites, and if so, do you know what type of precipitates they were?

R. Ploc—Yes, these regions were definitely associated with precipitates, which can be seen as small (<<1.0 μm) bumps in the center of the oxide mounds. Even after the oxide mounds had spalled, remnants of the precipitate effects could be clearly seen. No, we have not performed an extensive analyses on these precipitates, which appear to contain iron.

B. Cheng (GE)—You indicated that the oxidation behavior of zirconium in dry oxygen probably is similar to that in aqueous environments. Have you conducted testing in dry oxygen at higher temperature (approximately 500°C) to see if nodular corrosion will occur?

R. Ploc—The reason for stating that the oxidation behavior is similar is because the mechanism described is mainly mechanical in nature. However, that is not to say that there are not other mechanisms, perhaps even more important mechanisms occurring in aqueous environments. We have not conducted tests at approximately 500°C.

Mechanical Behavior, Stress Corrosion, and Fatigue

Link Between Stress Corrosion and Corrosion-Fatigue Behavior of Zircaloy in an Iodine Environment—ISABELLE SCHUSTER AND CLÉMENT LEMAIGNAN, pp. 535–547.

M. Leger (Ontario Hydro)—Could you provide additional details of the stresses in the fatigue cycle? When you have a stress corrosion mechanism operational, would not higher R ratios produce different effects?

C. Lemaignan—For all the fatigue tests performed, the R ratio = $\sigma_{min}/\sigma_{max}$ was always 0.1 (tension-tension). Higher R ratios were not tested but could have an effect on the value of K, for the intergranular to transgranular transition as seen for static tests and probably, on crack growth rate, but the effect should be small unless you go to very high values of R.

M. Noe (IAEA)—In your future work do you envision also including irradiation, which can not only modify the behavior of the metal but, more so, the aggressiveness of the iodine environment?

C. Lemaignan—This certainly would be of interest, but it is not an easy task. We will start with high-temperature tests and tests on cladding.

D. O'Boyle (Commonwealth Edison Co.)—One might expect, based on the data presented, some increase in crack growth in Zircaloy clad in nuclear plants operated in the load-following mode, especially in high burnup fuel. Has any effect of this been observed in the French load-following nuclear plants?

C. Lemaignan—From the large number of fuel rods that were operating under load follow in France, either in test reactors or in power plants, no failure could be attributed to fatigue. This may be due to the small stress range induced in the cladding during steady daily load follow and to the small number of cycles accumulated in this type of operation (less than 2000 cycles for very high burnup).

K. L. Murty (N. C. State University)—(1) How did you increase crack length during crack growth tests?

(2) What is the exponent in Paris' law, and what is the effect of I_2 on it?

C. Lemaignan—We followed the crack on the free surface using an optical microscope supported by a sliding beam. Crack growth was measured using an LVDT gage with an accuracy of 2 μm.

(2) The Paris' exponent was found to be about 4 for reference test. It was of similar value for crack growth rate ranges where the growth mechanism did not change (that is, pseudo-cleavage + ductile striations).

M. Nakatsuka (Nippon Nuclear Fuel Dev.)—Do your results still vary even as iodine concentration changes? I can not find striation in the fracture surface of fuel cladding tubes in high-cycle fatigue tests.

C. Lemaignan—We did not change the iodine concentration in our tests. Your results on cladding are very interesting and may lead to the assumption that a different mechanism may be active then.

Effects of Irradiation and Hydriding on the Mechanical Properties of Zircaloy-4 at High Fluence—ANAND M. GARDE, pp. 548–569.

B. Cox (AECL)—Do you have fractography on the low ductility Fort Calhoun fuel failure for which you showed a highly "stepped" crack? Such a crack indicates multiple initiation of subcracks and is very typical of iodine SCC cracks, but less so of hydride cracks. Since iodine fission products may be quite soluble in the silicone oil used to pressurize these fuel rods, detailed fractography would be needed to distinguish the cause of the cracks.

A. M. Garde—Fractography was not performed on the fuel cladding specimens. Although we cannot rule out the contribution of iodine SCC to the observed fracture process, because of the following factors, its contribution is expected to be insignificant. The fission gas release fraction for these rods was low, less than 1.33%. The absence of activity peaks at the pellet/pellet interfaces in the gamma scans indicated that the local gas release was also low. The power duty cycle experienced by these fuel rods was fairly modest and did not involve a power ramp. The application of stress during the burst testing was fairly uniform along the circumference and did not involve high localization of stress. In another investigation, we have observed "stepped" cracks associated with a hydriding pattern in an irradiated nonfueled rod with Zircaloy cladding. Detailed fractography on high burnup fuel cladding would be helpful to resolve this point.

C. Lemaignan (CEA Grenoble, France)—I am surprised that you could link the slip bands you observed in the tension tests (which are mostly caused by bulk properties like strain hardening and yield anisotropy), to dislocation channeling that is effective on a grain size scale. Could you comment on that?

A. M. Garde—Although we did not undertake electron microscopy in the current investigation to directly link the specimen surface slip bands with the microscopic dislocation channeling, previous investigators have suggested such a connection.

R. Dutton (AECL)—It is important to draw a distinction between dislocation channeling and deformation band formation. Thus, the Japanese work to which you refer shows that channeling occurs at all tension testing temperatures. It is uniformly distributed at the lower temperatures but is inhomogeneous, resulting in deformation bands, only at the temperature where RAH is operative. Do you know why RAH triggers localization of channeling to form deformation band and hence reduction in ductility?

A. M. Garde—The formation of a deformation band is due to the localization of dislocation channeling phenomenon. The localization of a dislocation channel occurs when work hardening does not take place in that channel. At low temperatures, work hardening occurs in each channel, thereby new channels are initiated and deformation band formation is not favored. At high temperatures (beyond the effective temperature range of RAH) when work hardening is weak or nonexistent, strain localization occurs in the channel leading to a low ductility failure.

R. B. Adamson (GE)—What was the gage length of the various specimens tested? We find that the uniform elongation in irradiated Zircaloy is very dependent on specimen geometry, which includes specimen gage dimensions and the resulting stress states created during deformation.

A. M. Garde—The cladding tube burst specimen length was 20 cm. The cladding tube tension specimen gage length was 5 cm. The guide tube dogbone tension specimen gage length was 2.5 cm. The guide tube ring tension specimen width was 1.25 cm. The effect of specimen geometry on the elongation of irradiated Zircaloy is well known. However, for the same burst specimen geometry and test conditions, we find change in elongation with increasing fluence.

K. L. Murty (N.C. State University)—(1) Is there a correlation between RAH and dips in ductility (RA)?

(2) What do you think is the effect of niobium additions to Zircaloy? Is it that niobium traps O_2 or reduces from the matrix?

(3) Do you find DSA (serrations) in Zircaloy?

A. M. Garde—There appears to be a correlation between RAH and the ductility minima. The flow stress peaks and ductility minima both are near the deformation temperature of 573 K. The effect of niobium addition to Zircaloy is a possible formation of Nb-O complexes with the radiation induced defects. The addition of niobium is expected to stabilize the oxygen-radiation defect complexes, thereby increasing the strength of RAH and delaying the localization of dislocation channels. Stress strain curve serrations caused by dynamic strain aging are generally not observed in Zircaloy. Weak serrations can be produced in Zircaloy at 1000 K [9].

R. B. Adamson (GE)—Do you have TEM results that describe the nature of the dislocation channels referred to in your paper? We have found that channeling occurs over a wide range of temperatures and fluences. Also the plane upon which the channeling occurs appears to be a function of the oxygen level and the degree of irradiation anneal hardening that occurs. Low oxygen levels promote basal plane channeling, and high oxygen promotes prism plane channeling.

A. M. Garde—We did not conduct TEM investigation. TEM investigation of deformed high fluence fuel cladding is highly desirable.

M. Nakatsuka (Nippon Nuclear Fuel Development)—How did you measure the failure strain after burst testing?

A. M. Garde—The failure strain after burst testing was obtained from photographs of a transverse metallographic mount of the maximum strain region of the burst specimen.

Y. Matsuo (Mitsubishi Metal Corp.)—Did you measure the oxide thickness of the specimens? In case of such high-burnup fuel rods, the oxide thickness may affect the calculation of cross-sectional area.

A. M. Garde—The oxide thickness on the fuel rods was measured at the poolside by eddy-current testing and was confirmed by metallography at the hot cell. The specimen cross-sectional area used to calculate the stress values did not include the area covered by the oxide layer.

H. M. Chung (Argonne National Laboratory)—In similar tube burst and expanding mandrel tests of several cold-worked and stress-relieved spent-fuel cladding at approximately 600 K, we noticed very few dislocation channels but a significant number of c-component dislocations (with indications of segregated oxygen) from TEM analysis (Ref 22, p. 568). It appeared to us that dislocation channeling is more likely for simple tension tests of recrystallized materials in particular but not for biaxial or multiaxial burst of stress-relieved material. It would be very interesting to conduct both TEM characterization and SEM fractographic analyses of the tube-burst cladding specimens of yours to confirm the density of the channel-plus-hydride features and absence of "nonductile" fractographic features, respectively. Our observation of ~5 nm-size oxide particles, which was shown to be bulk precipitates by means of stereomicroscopy [10], appears to be consistent with your observation of irradiation anneal hardening in commercial materials.

A. M. Garde—Although the extent of dislocation channeling is expected to be higher during the uniaxial tensile deformation of recrystallized material, Adamson et al. (Ref 38, p. 568) have observed dislocation channeling by TEM techniques after biaxial loading (closed end burst testing) of irradiated recrystallized Zircaloy-2 cladding. We agree that SEM characterization of fracture surfaces and TEM characterization of the microstructure of deformed specimens of highly irradiated Zircaloy would be helpful.

Applications of Crystallographic Textures of Zirconium Alloys in the Nuclear Industry—
K. LINGA MURTY, pp. 570–595.

R. Holt (Ontario Hydro)—Would you comment on the effect of rotation of the c axes about the z axis observed during recrystallization on the calculated anisotropy?

K. L. Murty—The R value is sensitive to the basal pole angle $\hat{\phi}$ and thus *slightly* increases following recrystallization anneal (which results in decreased $\hat{\phi}$): $R \approx \cot^2 \hat{\phi}$. However, the P parameter is very sensitive to recrystallization and increases significantly following recrystallization anneal (from approximately 2 in the cold worked state to approximately 7 for recrystallized material) [11].

E. Tenckhoff (Siemens/KWU)—How many pole figures were needed to deduce the ODF?

K. L. Murty—Two pole figures (basal and prism) will give an approximate ODF but a minimum of three pole figures is needed for a real representation of ODF of zirconium

alloys. Our experience shows that four or five pole figures give the CODF up to $l \sim 22$ but ODF-Euler plots are essentially identical to those derived from three pole figures with $l \leq 16$.

J. Harbottle—It is generally observed that creep in compression differs from creep in tension in CWSR Zircaloy Cladding. Does your model account for this difference in terms of a change in the predominantly basal slip which you find in tension? Also, how will this creep modelling be affected by irradiation?

K. L. Murty—Our model does not include the strength differential. All of the experimental data considered fall in the first quadrant with no compression and thus the model refers to the data in tension only. The change from the prism slip in recrystallized material to basal slip in CWSR is not due to tension since we considered the tensile data in both of these cases.

It should be noted that the CODF-CREEP model predicts the creep anisotropy and not the absolute values of the creep-rates. The analyses of the experimental results on irradiated Zircaloy cladding specimens from the Oconee reactor [12] indicate that, once the stress-free growth is accounted for, the creep anisotropy is unaffected by radiation exposure. In addition, these conclusions are supported by the data presented by Baty et al. [13] on CWSR (S1) and recrystallized (S2) Zircaloy-4. Thus, one needs to have an independent evaluation of the constant B in Eq 12 describing the irradiation creep-rate while our texture model provides the creep anisotropy for evaluating the creep-rates under any given stress state for the given textured cladding.

Creep and Growth

The Influence of Tin Content on the Thermal Creep of Zircaloy-4—WILLIAM A. MCINTEER, DAVID L. BATY, AND KIM O. STEIN, pp. 621–640.

A. M. Garde (Combustion Engineering)—Have you investigated the effect of tin on the in-reactor growth of Zircaloy-4?

W. McInteer—We are currently irradiating a series of rods with tin contents similar to the alloys discussed in this paper. We have not generated any irradiation growth data on these rods as of yet. There is a paper in the literature [14] that addresses the effect of tin on the irradiation growth rate. The major concern that we have in regards to growth is that the creep anisotropy may result in increased axial creep rates. The high stress creep test on the low-tin cladding exhibited a negative axial growth rate during internal pressurization tests. This will correspond to a positive axial growth rate during external pressurization. The positive axial growth rate will be additive to the irradiation growth and may indeed increase the axial growth on the fuel rods.

K. L. Murty (N.C. State University)—(1) Do you have plans to extend this work to recrystallized materials?

(2) What is the effect of tin on the temperatures and stress dependencies of the steady state creep rate?

W. McInteer—(1) We have done creep tests on other lots of recrystallized materials. The recrystallization, in general, decreases the creep rates, changes the shape of the creep locus significantly (high R and high P), and increases the stress dependence term. The use of recrystallized cladding for fuel rods is not being considered because of low tensile strengths.

(2) There did not appear to be any effect of tin on the activation energy or stress dependencies on these series of alloys. The tin had a good linear correlation with the A_g term in the creep model.

Y. Matsuo (Mitsubishi Metal Corp.)—(1) In our experience there is a good relationship between CSR and Kern's factor, but in your data Lots A and G have rather high CSR value in spite of Kearn's factors similar to other lots. Do you have any idea why the difference occurred?

(2) Did you analyze the oxygen contents of the materials? Did you find any correlation between oxygen level and creep properties?

W. McInteer—(1) The CSR values on our standard product typical range from 1.90 to 2.20. The CSR value Lot A is outside our normal range. Lot A, however, has the highest amount of tin, and there could possibly be an affect of tin on the room temperature deformation.

(2) Oxygen was not a variable in this investigation. Oxygen contents in the claddings were at nominal levels ranging from 1150 to 1350 ppm. There did not appear to be any affect on the steady state creep rate over this narrow range.

M. Nakatsuka (Nippon Nuclear Fuel)—We observed a reduction of plastic anisotropy of BWR fuel cladding tubes because of neutron irradiation. Do you think that the effect of tin content on creep rate will still remain after irradiation?

W. McInteer—We have found that the anisotropy is a function of the strain rate and temperature. We have not performed thermal creep tests after irradiation. Our post-irradiation examination data, however, suggest that the thermal creep anisotropy is similar to the irradiation creep anisotropy and does not seem to change with irradiation.

J. Harbottle (CEGB)—You remarked that your results indicate that the reduction of the tin content in order to improve corrosion resistance may adversely affect the creep resistance. This could be presumably counteracted by the addition of other matrix strengthening elements such as iron as observed in the ZIRLO alloy.

Would you comment on the creep behavior of your alloy "H," which had a markedly lower radial texture?

W. McInteer—Lot H was produced by a second vendor using a lower final anneal temperature and had a lower tin content (1.34%). The creep behavior of this lot was in the same general range of the standard production cladding (Lots A through D) suggesting that the effect of tin may be somewhat reduced with less radial texture and lower anneal temperatures. However, it is difficult to separate the effect of texture caused by the fact no control sample was tested. Our experience has shown that the less radially textured claddings typically have higher P values, which correspond to increased creep strength for the 2:1 stress state whereas the lower anneal temperature and low tin tend to decrease creep strength.

As far as ZIRLO alloy is concerned, the major creep strengtheners are the tin and the niobium. Iron is less effective in increasing the creep strength.

Effects of High Neutron Fluences on Microstructure and Growth of Zircaloy-4—FREDRICH GARZAROLLI, PETER DEWES, GERD MAUSSNER, AND HANS-HENNING BASSO, pp. 641–657.

M. Griffiths (Chalk River Nuclear Labs)—You showed a growth curve indicating saturation of growth for cold-worked material with increasing fluence. Can you comment on the

resultant microstructure? Does the saturation correspond with recovery of the dislocation network? What is the final structure?

F. Garzarolli—The most evident change in the microstructure is the formation of subgrains, however we have not analyzed the microstructure to an extent that would be necessary to make a definite statement.

R. A. Holt (Ontario Hydro)—(1) Are the grains flattened and elongated in the stress relieved materials, and in what section and in what direction are the grain shapes measured?

(2) Did the carbon content correlate with the grain size and were you able to separate the effects of carbon content and grain size?

(3) In the highly irradiated stress relieved materials did the *C*-component dislocations have the same straight parallel appearance as in the annealed material, or are they curved and not parallel to the basal plane as in archive cold-worked and stress-relieved material?

F. Garzarolli—(1) The grains of stress relieved tubes were elongated. The evaluation of the grain size was done only in the cross section of the tubes.

(2) The wide variation of grain size is only due to different fabrication parameters and does not correlate with the carbon content.

(3) At 300°C, *C*-component dislocations in stress relieved material were both straight and curved. We did not evaluate their nature and extent, to give a ratio between *C*-component and *A*-dislocations.

R. B. Adamson (GE)—What was the quenching rate of your beta-quenched material? Did you see the same type and morphology of $Zr_4(FeCr)$ precipitates that form when the quenching rates are several 100°C/s (as reported yesterday)?

F. Garzarolli—The beta-quenching rate of the Sample 5 (Lot 2) was roughly 20 K/s, and therefore much smaller than the material presented in the paper "Beta-Quenched Zircaloy-4: Effects of . . ." presented during this meeting. We did not identify the crystal structure of the precipitates in Sample 5 (Lot 3), but from other studies on samples with comparable beta-quenching rates we deduce that the particles are Laves phases.

Effects of Microstructural Factors on Irradiation Growth in Zirconium-Niobium Alloys— NORIYUKI SADAOKA AND MOTOMASA FUSE, pp. 692–704.

R. A. Holt (Ontario Hydro)—Could you comment on the reliability of the anisotropies calculated for the point defect migration energies, particularly the interstitials in their different configurations?

M. Fuse—The molecular dynamic calculations strongly rely on the interatomic potential for its validity. In the present calculation the potential was determined by fitting it to elastic constants of the zirconium, which is the standard method developed by Dr. R. A. Johnson. I think this method gives a fairly good interatomic potential at present compared with the other methods.

Qualitative features of point defect properties are reasonably described by the interatomic potential. Originally, point defect properties in fcc and bcc crystals, such as interstitial configurations, have been evaluated by using the molecular dynamic method, and it could have predicted the correct behaviors. Though there is no assurance that it can treat the

point defects in hcp crystals as in fcc and bcc, we have a good stance to believe that it gives a view corresponding to the real situation.

The present growth model does not include the concepts of diffusional anisotropic difference. Therefore, only the average value of migration energies has been used for solving the rate equations of point defects. In the present status of molecular dynamic calculations, the precise values, such as migration energies, can not be considered to be right. Therefore we should treat the values as a reference frame for evaluating the growth rate under a circumstance that the detailed evaluations of point defect properties are not completed by experimental approaches.

R. Dutton (AECL)—If I understood correctly, although your point defect calculations indicated an anisotropy in interstitial migration, you have to ignore this via an averaging of the energies. Based on Canadian work in this area, it would appear that anisotropy should be included in zirconium deformation models.

M. Fuse—In the present growth model, an anisotropy of point defect migration in hcp crytal is neglected. The purpose of the present calculation is to clarify the point that the growth model without the concept of diffusional anisotropic difference can predict one of the anomalous growth behaviors of Zr-2.5 wt% Nb alloys.

I feel that all of the present growth models are in the same situation in the sense that the elementary processes of point defects are not clarified on the experimental basis. So, we should check if there are inconsistencies in the model for screening its applicability to predict the various growth behaviors.

C. Lemaignan (CEA Grenoble, France)—Referring to previous questions on potential and anisotropy, are you able to obtain a good value of the c/a parameter with just a pair potential?

M. Fuse—In the present molecular dynamic calculations, the c/a ratio of the hcp zirconium crystal has been kept to be ideal. I have not yet ascertained whether the real c/a ratio can be obtained by using the adopted interatomic potential.

Regarding the anisotropy of interstitials migration, the smaller c/a ratio is expected to give easier migration of an interstitial along the c axis because of the potential barrier configuration towards the basal plane. So, I am expecting that the essential features on the point defect anisotropy would not be changed drastically even if the real c/a ratio is adopted for the calculations.

V. Fidleris (AECL)—What temperature dependence of growth does your model predict for Route 1 and the standard type of Zr-2.5Nb material, bearing in mind that there is (to be published) evidence to show that the Route 1 material exhibits normal growth behavior at 330 K.

M. Fuse—The essential point of the present growth model is that the interstitials produced in a grain are strongly absorbed by the grain boundary because of the presence of both twist and tilt low-angle boundaries and the thinner layer. The inflow rate of interstitials into the grain boundaries is described by the diffusion constant and the concentration gradient at the boundary. In the case of a thin layer, the effective concentration gradient of interstitials occurs in the thinner direction. In the ordinary grain with isotropic shape the concentration in the grain is determined mainly by the dislocations.

Because of the situation mentioned above, the ratio Ra of absorption rate by the grain boundary to the absorption rate by the dislocation is enhanced in the case of a grain with

a thin layer compared with the case of an ordinary grain. Temperature affects both absorptions by grain boundaries and dislocations. In the case of low temperature, the absorption by the dislocation results in the reduction of the ratio Ra. This can explain the behavior of Route 1 specimens in the experiments of Perker et al.

The Effect of Temperature on the Irradiation Growth of Cold-Worked Zr-2.5 wt% Nb—
RICHARD A. HOLT AND RONALD G. FLECK, pp. 705–724.

M. Fuse (Energy Research Lab, Hitachi Ltd.)—Does anisotropy of point defect diffusion depend on an experimental basis?

R. A. Holt—There is direct evidence for anisotropic vacancy migration in alpha-zirconium, however, there is no direct evidence for anisotropic SIA migration. Note that it is the difference in anisotropy of migration between the vacancy and SIA and not the absolute degree of anisotropy in either case that is important.

D. O. Northwood (University of Windsor)—Can the differences in behavior of "standard" and "modified" material be related to the differences in distribution of the beta-phase, that is, continuous or semicontinuous in "standard," and discrete particles in "modified" material?

R. A. Holt—It is possible that the differences in behavior of the "standard" and "modified" materials are influenced by the different morphologies of the beta-phase. However, there is a parallel between the effect of increasing temperature and the difference in behavior between the "standard" and "modified" materials. This appears to support our suggestion that the differences in grain size and dislocation density are sufficient to explain the differences in the growth behavior via the DAD effect.

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