THE HISTORY OF LOCA EMBRITTLEMENT CRITERIA

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Abstract

Performance of high-burnup fuel and fuel cladding fabricated from new types of alloys (such as Zirlo, M5, MDA, and duplex alloys) under loss-of-coolant-accident (LOCA) situations is not well understood at this time. To correctly interpret the results of investigations on the performance of the old and new types of fuel cladding, especially at high burnup, it is necessary to accurately understand the history and relevant databases of current LOCA embrittlement criteria. In this paper, documented records of the 1973 Emergency Core Cooling System (ECCS) Rule-Making Hearing were carefully examined to clarify the rationale and data bases used to establish the 1204°C peak cladding temperature and 17% maximum oxidation limits. A large amount of data, obtained for zero- or low-burnup Zircaloy cladding and reported in literature only after the 1973 Rule-Making Hearing, were also evaluated and compared with the current criteria to better quantify the margin of safety under LOCA conditions.

1. Introduction

Because of major advantages in fuel-cycle costs, reactor operation, and waste management, the current trend in the nuclear industry is to increase fuel discharge burnup. At high burnup, fuel rods fabricated from conventional Zircaloys often exhibit significant degradation in microstructure. This is especially pronounced in pressurized-water reactor (PWR) rods fabricated from standard Zircaloy-4 in which significant oxidation, hydriding, and oxide spallation can occur. Thus, many fuel vendors have developed and proposed the use of new cladding alloys, such as low-tin Zircaloy-4, Zirlo, M5, MDA, duplex cladding, and Zr-lined Zircaloy-2. Performance of these alloys under loss-of-coolant-accident (LOCA) situations, especially at high burnup, is not well understood at this time. Therefore, it is important to verify the safety margins for high-burnup fuel and fuels clad with new alloys. In recognition of this, LOCA-related behavior of various types of high-burnup fuel cladding is being actively investigated in several countries [1-6]. However, to correctly interpret the results of such investigations, and if necessary, to establish new embrittlement thresholds that maintain an adequate safety margin for high-burnup operation, it appears necessary to accurately understand the rationale, history, and data bases used to establish the current LOCA criteria, i.e., maximum cladding temperature limit of 1204°C (2200°F) and maximum oxidation limit of 17%. For this purpose, documented records of the 1973 Atomic Energy Commission (AEC) Emergency Core Cooling System (ECCS) Rule-Making Hearing were carefully examined and the relevant databases were reevaluated in this paper. Since the establishment of the current criteria, large amounts of data were obtained in many countries for zero- or low-burnup fuel cladding. The results of these investigations were also critically evaluated to determine the validity of the current criteria and safety margins for a wider range of conditions.

2. Primary Objectives of Current Criteria

In 1967, an Advisory Task Force on Power Reactor Emergency Cooling [7], appointed to provide "additional assurance that substantial meltdown is prevented" by core cooling systems, concluded that:

> "The analysis of (a LOCA) requires that the core be maintained in place and essentially intact to preserve the heat-transfer area and coolant-flow geometry. Without preservation of heat-transfer area and coolant-flow geometry, fuel-element melting and core disassembly would be expected... Continuity of emergency core cooling **must be maintained after termination of the temperature transient for an indefinite period until the heat generation decays to an insignificant level**, or until disposition of the core is made."

This rationale makes it plainly clear that it is most important to preserve the heat transfer area and the coolant flow geometry not only during the short-term portion of the core temperature transient but also for long term.

Consistent with the conclusions of the Ergen Task Force, the U.S. Atomic Energy Commission (AEC) promulgated Criterion 35 of the General Design Criteria [8] which states that: "... fuel and clad damage that could interfere with **continued effective core cooling** is prevented." It also promulgated Criterion 3 of the Interim Acceptance Criteria for ECCS for LWR [9] which states that: "The clad temperature transient is terminated at a time when the core geometry is still amenable to cooling, and before the cladding is so embrittled as to fail **during or after quenching**."

These criteria were subjected to a Rule-Making Hearing in 1973, which was extensively documented in the Journal of Nuclear Safety in 1974 [10,11]. During the hearing process, the last part of the Criterion 3 was replaced by the modified Criterion 1 and the new Criterion 2 of the Code of Federal Regulations, Title 10, Part 50.46, Article (b), commonly referred to as 10 CFR 50.46 [12]. Thus, the AEC Commissioners wrote:

> "In view of the fundamental and historical importance of maintaining core coolability, we retain this criterion as a basic objective, in a more general form than it appeared in the Interim Acceptance Criteria. It is

> not controversial as a criterion… Although most of the attention of the ECCS hearings has been focused on the events of the first few minutes after a postulated major cooling line break, up to the time that the cladding would be cooled to a temperature of 300°F or less, the **long-term maintenance of cooling** would be equally important [13]."

There are two key factors to consider to evaluate the change in coolable geometry of core, a brittle mode and a ductile mode of deformation in fuel cladding. The ductile mode is related to cladding ballooning, burst, and coolant channel blockage. This mode will not be treated in this paper. Our focus in this paper is on the change in coolable geometry due to cladding embrittlement and failure.

3. Metallurgy of Cladding Embrittlement

In 1960s, Wilson and Barnes performed laboratory tests simulating steam reactions with Zircaloy-clad fuel rods at high temperatures. They observed embrittlement of oxidized cladding well below the melting temperature of Zircaloy, either during the test itself or during removal of the specimen from the oxidizing furnace. The results were reported in Argonne National Laboratory (ANL) progress reports and synthesized later in Ref. 14. At the same period, investigators in Oak Ridge National Laboratory (ORNL) conducted TREAT Test No. 6 with Zircaloy cladding in steam and observed that the specimen was severely embrittled by oxidation [15]. Also at about the same period, many tests were conducted that simulated reactivity-initiated accident (RIA) in SPERT-CDC and TREAT reactors. Results of metallurgical examination in these tests showed that embrittlement was caused by severe microstructural modification of the cladding. Brittle cladding cross sections exhibited oxide layer, oxygen-stabilized alpha-phase layer and a region of acicular prior beta-phase. The results were later reported by Fujishiro et al. [16].

As a result of these observations, the scientific community was alerted to the fact that oxidation of Zircaloys above the alpha-to-beta transformation temperature results in the formation of inherently brittle phases, i.e., Zr oxide, oxygen stabilized alpha-Zr (fcc structure), and diffusion of oxygen into the underlying beta phase (bcc structure). This is shown schematically in Fig. 1. Ductility of cladding could be severely degraded if the degree of oxidation is high. It was also realized that, if the embrittled cladding fragments into small pieces, the coolability of the core could be seriously impaired.

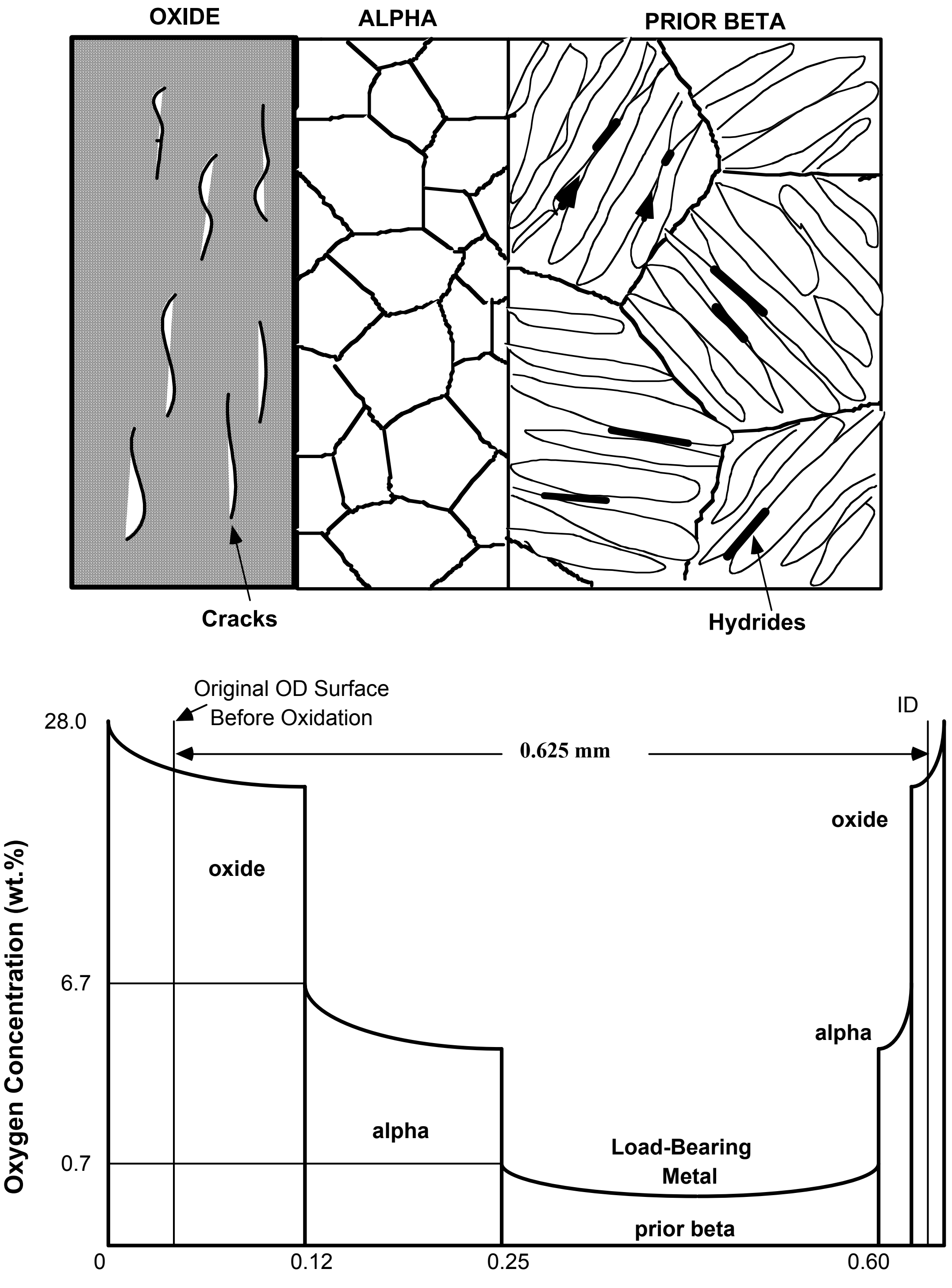


Fig. 1. Schematic illustration of microstructure (top) and oxygen distribution (bottom) in oxide, stabilized alpha, and prior-beta (transformed-beta) layers in Zircaloy cladding after oxidation near 1200°C.

Significantly embrittled cladding can fragment during the quenching phase of a LOCA. The action of rewetting by ECCS water involves the collapse of the vapor film that covers the cladding outer-diameter (OD) surface prior to subsequent transition to nucleate boiling. This event takes place at a more or less constant temperature, i.e., the Leidenfrost temperature. For oxidized Zircaloy-4 cladding rewetted by bottom-flooding water, ANL investigators reported that rewetting occurs in the range of 475-600°C [17]. The abrupt change in the heat transfer conditions induces large thermal-shock stress, which can fracture the cladding, if it is sufficiently embrittled by oxidation.

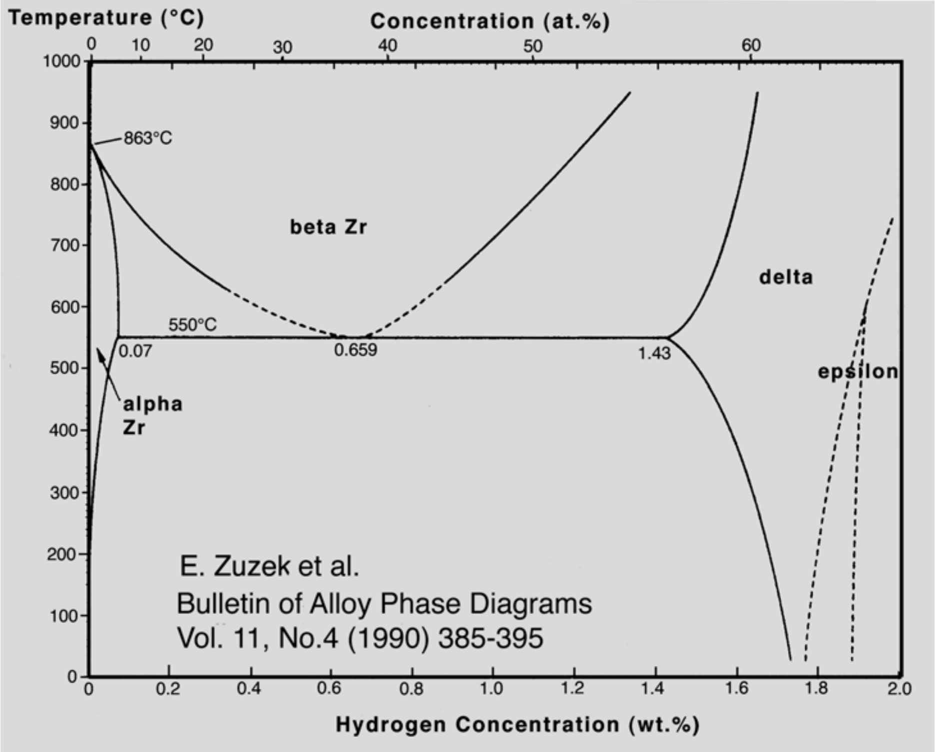
Below the Leidenfrost temperature, there is continued risk of fragmentation after quenching. In accordance with the opinions of the Ergen Task Force and the AEC staff and commissioners mentioned earlier, other experts also wrote a similar opinion for OECD Committee on Safety of Nuclear Installations (CSNI) [18]: "The ability of the cladding to withstand the thermal-shock stresses of quenching during rewetting **or post-LOCA forces** is related to the extent and detailed nature of oxidation during the transient. **The post-LOCA forces, which need to be taken into account, are the hydraulic, seismic, handling, and transport forces.**"

There are two primary factors that exacerbate the susceptibility of oxidized cladding to post-quench embrittlement in comparison with susceptibility to fragmentation during quenching: i.e., (1) more pronounced effect of oxygen dissolved in beta phase at lower temperature of loading (i.e., more pronounced after quench than during quench) and (2) more pronounced effect of hydrogen uptake which may occur during irradiation (e.g., in high-burnup Zircaloy-4) or during transient oxidation in steam (e.g., from cladding inner surface in contact with stagnant steam near a ballooned and burst region). For cooling rates typical of bottom flooding of core (i.e., 1-5°C/s), most hydrogen atoms remain in solution in the beta phase at Leidenfrost temperature, and in such state, hydrogen has little effect on the fracture resistance of an oxidized Zircaloy. However, when load is imposed at temperatures below the Leidenfrost temperature, precipitated hydrides strongly influence the fracture resistance of cladding. Eutectoid decomposition of hydrogen-stabilized beta phase at temperatures below ≈550°C [19] is the major factor that causes this deleterious effect (see Fig. 2).

4. Opinion of Regulatory Staff and Commissioners during 1973 Rule-Making Hearing

4.1 Reluctance to Neglect Effects of Mechanical Constraints

Some factors during a LOCA, such as ballooning of the rod near the spacer grid, rod-grid spring chemical interaction, and the friction between the fuel rod and spacer grids, can restrict the axial movement of the cladding. Also, guide tubes in a PWR fuel assembly are mechanically fixed to the spacer grids. Because of these factors, fuel rods during reflooding will be subject to tensile load that is produced due to the differential axial shrinkage between a cladding and the guide tube. Rods may interact each other due to ballooning or bowing. For high-burnup fuels in which tight pellet-cladding bonding is common, axial shrinkage can be restricted if the tight bonding remains unchanged after ballooning and burst. These constraints will remain after quench, when deleterious effects of oxygen and hydrogen are far more pronounced.



E. Zuzek et al.
Bulletin of Alloy Phase Diagrams
Vol. 11, No.4 (1990) 385-395

Figure 2.

Zr-H binary phase diagram (from E. Zuzek et al., Bulletin of Alloy Phase Diagrams, Vol. 11, No. 4, 1990, pp. 385-395).

In recognition of this, the AEC Staff wrote during the 1973 Rule-Making Hearing that "**the loads due to assembly restraint and rod-to-rod interaction may not be small compared to the thermal shock load and cannot be neglected** [20]." Subsequently, it was concluded that: "The staff believes that quench loads are likely the major loads, but **the staff does not believe that the evidence is as yet conclusive enough to ignore all other loads** [21]."

Then, the Commissioners added: "**There is some lack of certainty as to just what nature of stresses would be encountered during the LOCA**.... (We want) to draw attention to the fact that **it may not be possible to anticipate and calculate all of the stresses to which fuel rods would be subjected in a LOCA**. Although we believe the calculations of thermal shock stresses are worthwhile and informative, we agree with the regulatory staff that they are not sufficiently well defined to depend on for regulatory purposes [13]."

Before 1973, no thermal-shock quench test was performed on mechanically constrained cladding specimens. Then in early 1980s, Uetsuka et al. performed quenching tests on cladding sections under severely constrained condition [22]. In their experiment, cladding tube was fixed at the bottom but was allowed to freely elongate in axial direction during oxidation at high temperature. As a result, cladding length increased freely because of thermal expansion and oxide-induced creep. At the end of the isothermal oxidation, the specimen top was fixed to the crosshead of an Instron tensile facility. Then, the load-time curve was continuously monitored during quenching. Thus, at Leidenfrost temperature, the cladding tube was subjected to combined axial-tensile and thermal-shock stresses. The results of the tests are summarized in the Fig. 3. Similar tests were also performed on unconstrained tubes (Fig. 4).

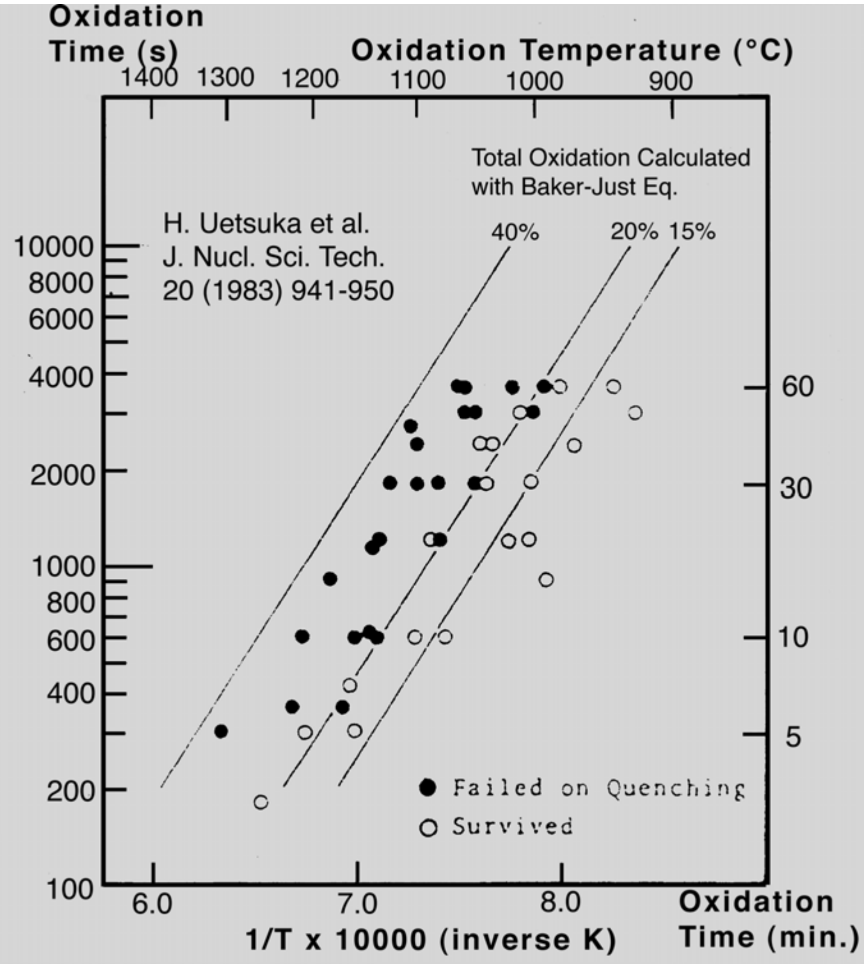


Figure 3.

Failure-nonfailure boundary for fully constrained Zircaloy-4 after oxidation in steam and quenching as function of oxidation time and temperature; total oxidation calculated with Baker-Just equation is also indicated (from Uetsuska et al., J. Nucl. Sci. Tech. 20, 1983, pp. 941-950).

A comparison of the results from the two contrasting types of test shows a large effect of the mechanical constraint. However, it is difficult to conclude whether the degree of constraint in the experiments of Uetsuka et al. is prototypic of a LOCA or unrealistically too severe. The 17% oxidation limit, calculated with Baker-Just correlation, appears to be adequate for protection of constrained rods against thermal-shock failure (Fig. 3), whereas a large margin is evident for unconstrained rods (Fig. 4).

Unlike other bundle tests such as NRU, REBEKA, JAERI and ORNL multirod tests that were entirely devoted to the study of ballooning, burst, and flow-channel blockage, some of the tests in Phebus LOCA program was devoted to the study of embrittlement [23]. The fragmented Rod 18 of the Test 219, exposed to ≈1330°C, is especially interesting (see Fig. 5). For this oxidation temperature, results of calculation with PRECIP-II Code [24] indicates that the O content in the beta phase was higher than 0.9 wt.%, a threshold O concentration found to be associated with thermal-shock failure or survival [17]. Rod 18 fragmented despite it was oxidized to an equivalent-cladding reacted (ECR) value of only ≈16%. This observation indicates a deleterious bundle effect, i.e., an additional mechanical constraint.

As a conclusion, results of the JAERI constraint quench test and the PHEBUS-LOCA Test appear to justify the reluctance of the AEC staff and commissioners to neglect the effect of mechanical constraints on the susceptibility to thermal-shock failure.

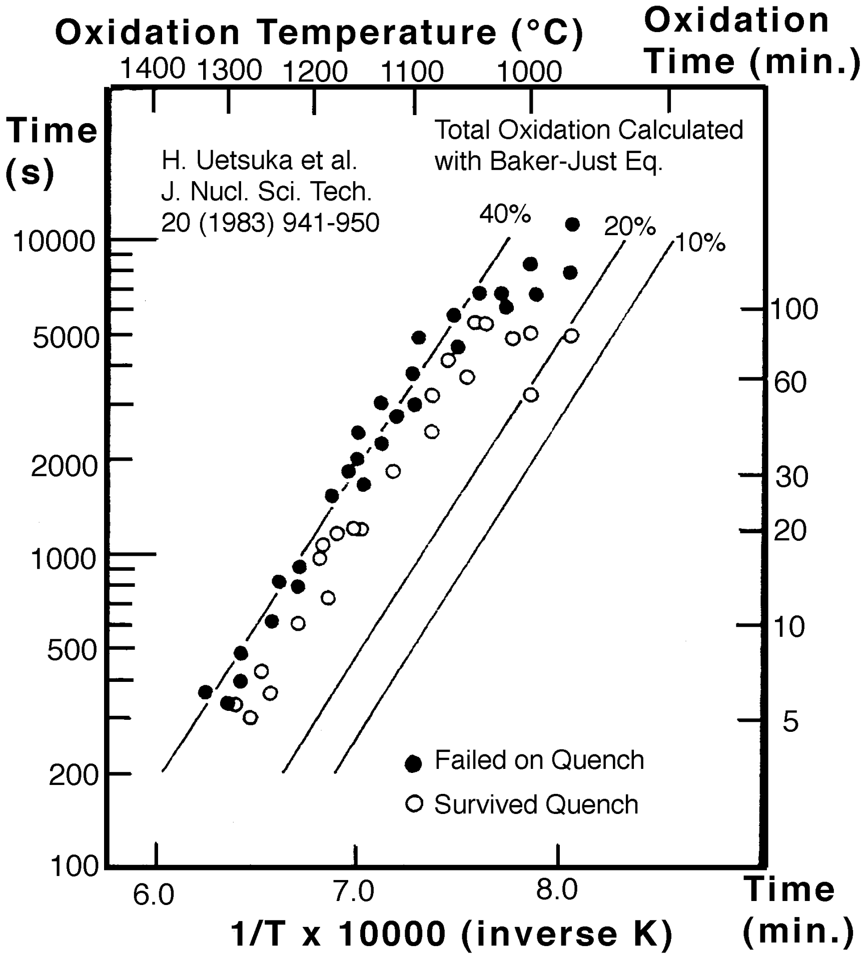


Figure 4.

Failure-nonfailure boundary for unconstrained Zircaloy-4 after oxidation in steam and quenching as function of oxidation time and temperature; total oxidation calculated with Baker-Just equation is also shown (from Uetsuska et al., J. Nucl. Sci. Tech. 20, 1983, pp. 941-950).

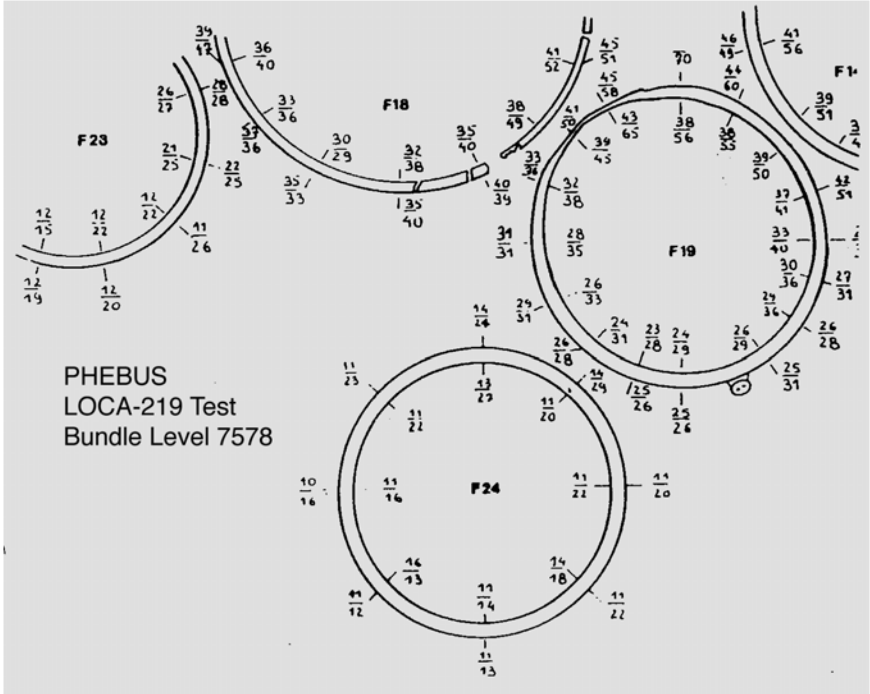


Figure 5.

Cross-section of portion of fuel assembly from PHEBUS LOCA-219 Test (Ref. 23), showing fragmentation of cladding.

4.2 Preservation of Ductility and Consideration of Results from Unconstrained Quench Test

At the end of the 1973 Hearing, the AEC Commissioners wrote: "...Nevertheless we find the quench results encouraging in that they provide assurance that the 2200°F limit is conservative. Our selection of the 2200°F limit results primarily from **our belief that retention of ductility in the Zircaloy is the best guarantee of its remaining intact during the hypothetical LOCA**... The thermal shock tests are reassuring, but **their use for licensing purposes** would involve an assumption of knowledge of the detailed process taking place in the core during a LOCA **that we do not believe is justified** [13]."

Without much ambiguity, this conclusion clearly expressed the belief that retention of ductility was considered the best guarantee against potential fragmentation under various types of loading (thermal-shock, bundle constraints, hydraulic, handling, and seismic forces). During the 1973 Hearing, results from unconstrained quench tests (simple thermal-shock test) were considered only corroborative and reassuring. However, their use for regulatory purposes was not accepted.

Results of later investigations on unconstrained or partially constrained cladding [17,18] showed a large margin of survival under thermal shock relative to 17%-ECR and 2200°F (1204°C) peak temperature limits. Such results are summarized in Fig. 6. No fragmentation occurred for ECR < 17% for all oxidation temperatures, whereas significant margin of survival was observed for oxidation temperatures <1204°C. The results in Fig. 6 were limited for thermal-shock tests in which cladding tube or ring was directly quenched from the maximum oxidation temperature without slow cooling through the range of beta-to-alpha-prime transformation. For slow-cooling conditions, more pronounced margin of survival was observed [17].

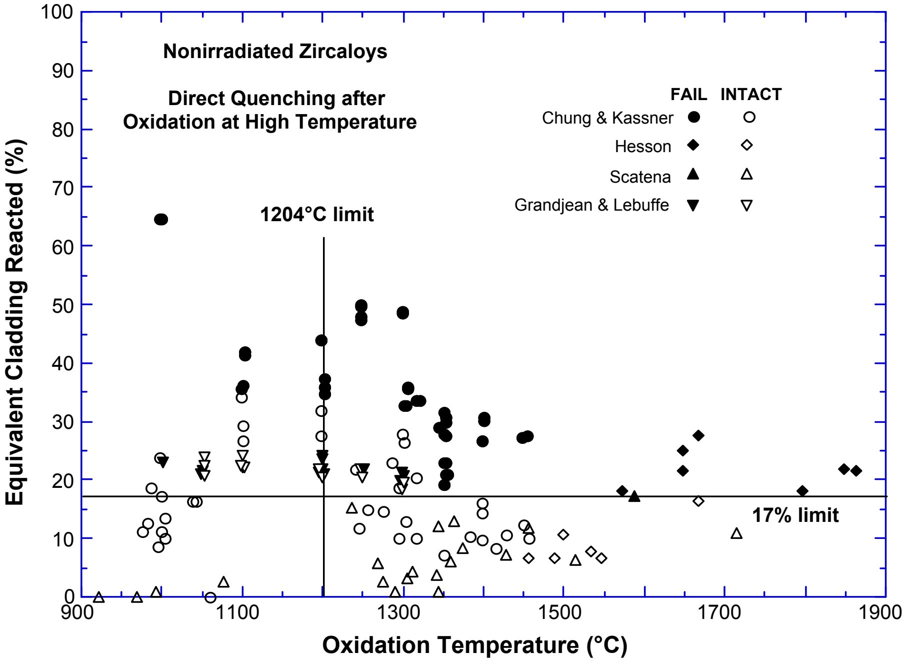


Figure 6.

Failure boundary of partially constrained Zircaloy cladding tubes or unconstrained rings after oxidation at high temperature and direct quenching from peak oxidation temperature (from Refs. 17 and 29).

5. 17%-Oxidation Criterion

5.1 Establishment of 17% Criterion During 1973 Rule-Making Hearing

The rationale for establishment of the two criteria in 10 CFR 50.46(b) is described in this section. As indicated in a few reports [17,18] that reviewed the results of the LOCA-related tests performed before and after the 1973 Hearing, the 17%-ECR and 1204°C criteria were primarily based on the results of post-quench ductility tests conducted by Hobson [25,26].

Figure 7 summarizes the results of Hobson's ring compression tests performed at 23-150°C. Zircaloy-4 cladding tubes were oxidized in steam on two sides, followed by direct quenching into water. Then, short ring specimens cut from the oxidized tube were either compressed slowly to a total deflection of 3.8 mm or squashed by impact loading. After the test, the broken pieces of the ring was assembled back to determine the degree of brittleness. Zero ductility was defined on the basis of the macroscopic geometry of the broken pieces and the morphology of the fracture surface on microscopic scale. Each data point in Fig. 7 indicates failure type, test identification number, oxidation time in min., oxidation temperature in °F, and first maximum load in pound.

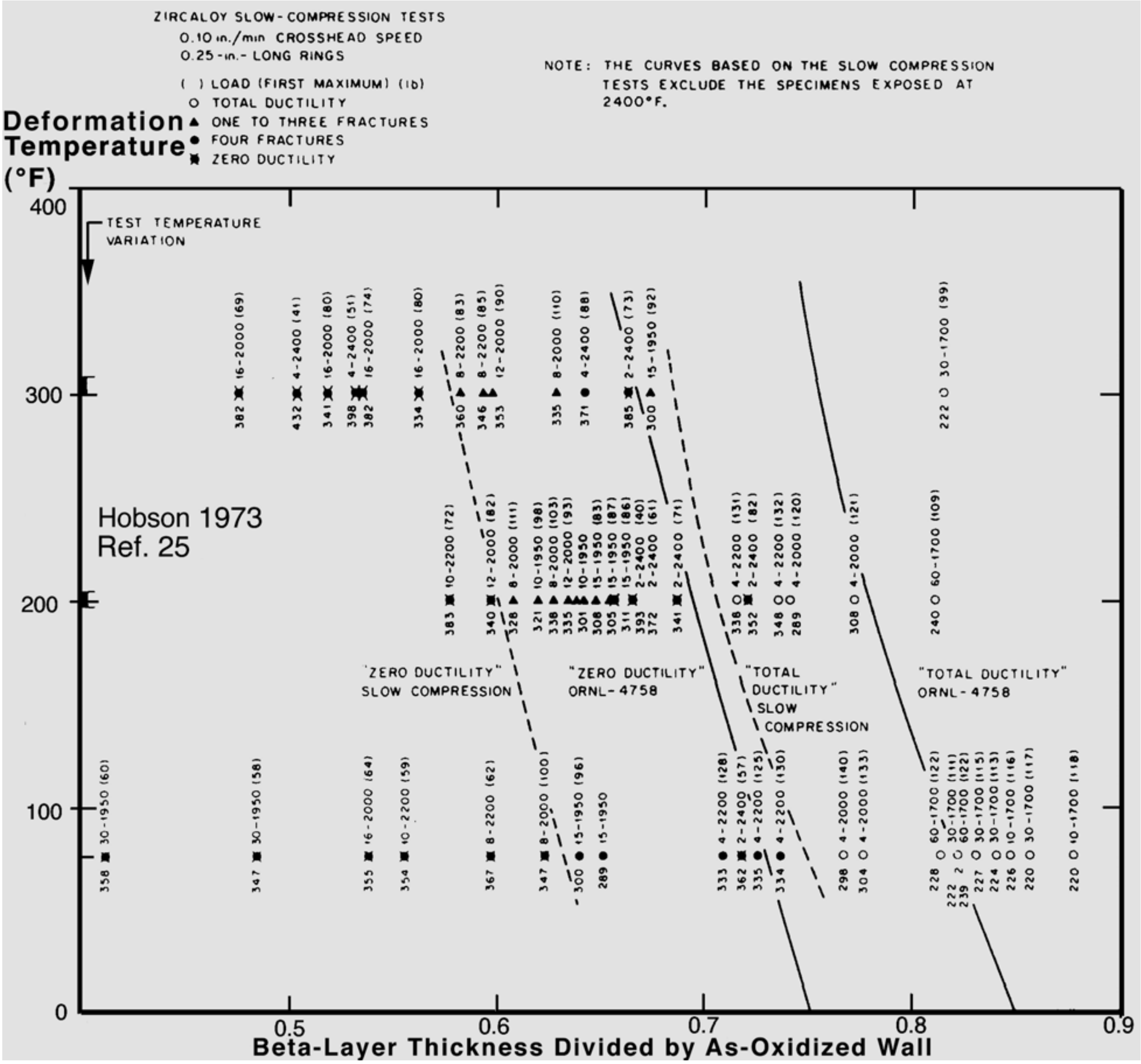


Figure 7.

Ductility of two-side-oxidized Zircaloy rings as function of slow- or fast-compression temperature and fraction of transformed-beta-layer (from Hobson, Ref. 25 and 26).

The dashed line on the left side of Fig. 7 denotes the zero ductility domain for slow-compression rate. This domain is valid only for oxidation temperatures of <2200°F or <1204°C. During the 1973 Hearing, ORNL investigators suggested to consider a zero-ductility temperature (ZDT) no higher than the saturation temperature during reflood, i.e., ≈135°C. Zero-ductility threshold at this temperature is equivalent to a beta-layer fraction of ≈0.58, or a fraction of combined oxide layer plus alpha layer thickness (defined as X_T) of ≈0.42 (based on as-oxidized cladding wall). The latter fraction corresponds to ≈0.44 if it is calculated based on fresh nonoxidized cladding wall (defined as Wo).

The threshold fractional thickness of the combined oxide and alpha layer (X_T/Wo, defined as Xoa in Fig. 8) of 0.44, which corresponds to zero ductility threshold for slow compression at 135°C, was the key number in the establishment of 17% oxidation criterion in the 1973 Hearing. During the hearing, the AEC Regulatory Staff wrote:

> "Giving due credit to the numerous quench experiments and the ORNL zero ductility experimental data points for both impact and slow compression, the staff suggests that an embrittlement criterion be based on a **calculated X_T/Wo that shall not exceed 0.44. This is equivalent to a zero ductility temperature of about ... 275°F based on the slow compression tests** [20]."

Then, it was concluded:

> "To preclude clad fragmentation and to account for effects noted in the tests described above, **a limit of X_T/Wo ≤ 0.44** was earlier suggested by the Regulatory staff as an embrittlement criterion (Exhibit 1113, page 18-18). This limit was inferred from quench tests and mechanical tests. Criterion (b)(2) is now proposed as a better method of specifying a similar limit on the extent of cladding oxidation. The bases for proposing this method are described below: (The) use (of the **17 percent reaction limit) with the Baker-Just equation** is conservative when compared to the previously suggested limits of **X_T/Wo ≤ 0.44**. This is shown in Figure 8 (of this paper) for isothermal conditions. Four lines of **constant calculated X_T/Wo** (two for 0.44 and two for 0.35) are constructed on the plot of percent reaction versus a parameter proportional to the square root of exposure time. The solid X_T/Wo lines are based on Pawel's equation (Exhibit 1133) (Ref. 27 of this paper), and the dashed lines are based on Exhibit 09, page 9, Figure 5 (Ref. 25 of this paper). As can be seen, **the X_T/Wo = 0.44 lines are both above the 17 percent reaction line...**"

Results of a total of five key tests and calculations are summarized in Fig. 8, a complex but the most important step used to reach the 17% oxidation limit. They are: (1) equivalent cladding reacted (ECR) calculated as function of oxidation temperature and square root of time based on Baker-Just correlation, (2) two broken curves which define the time and temperature to reach the threshold fractional thickness of the combined oxide and alpha layer (denoted as Xoa) of 0.44 and 0.35, as determined based on the data given in Ref. 25, Page 9, Fig.5, (3) two solid curves that define the time and temperature to reach the threshold fractional thickness of the combined oxide and alpha layer of 0.44 and 0.35, as determined based on the method of Ref. 27, (4) six ECR-(time)$^{0.5}$

curves from the thermal-shock tests of Hesson et al., Ref. 14, and (5) results from Combustion Engineering (CE) ring compression tests after one-sided oxidation.

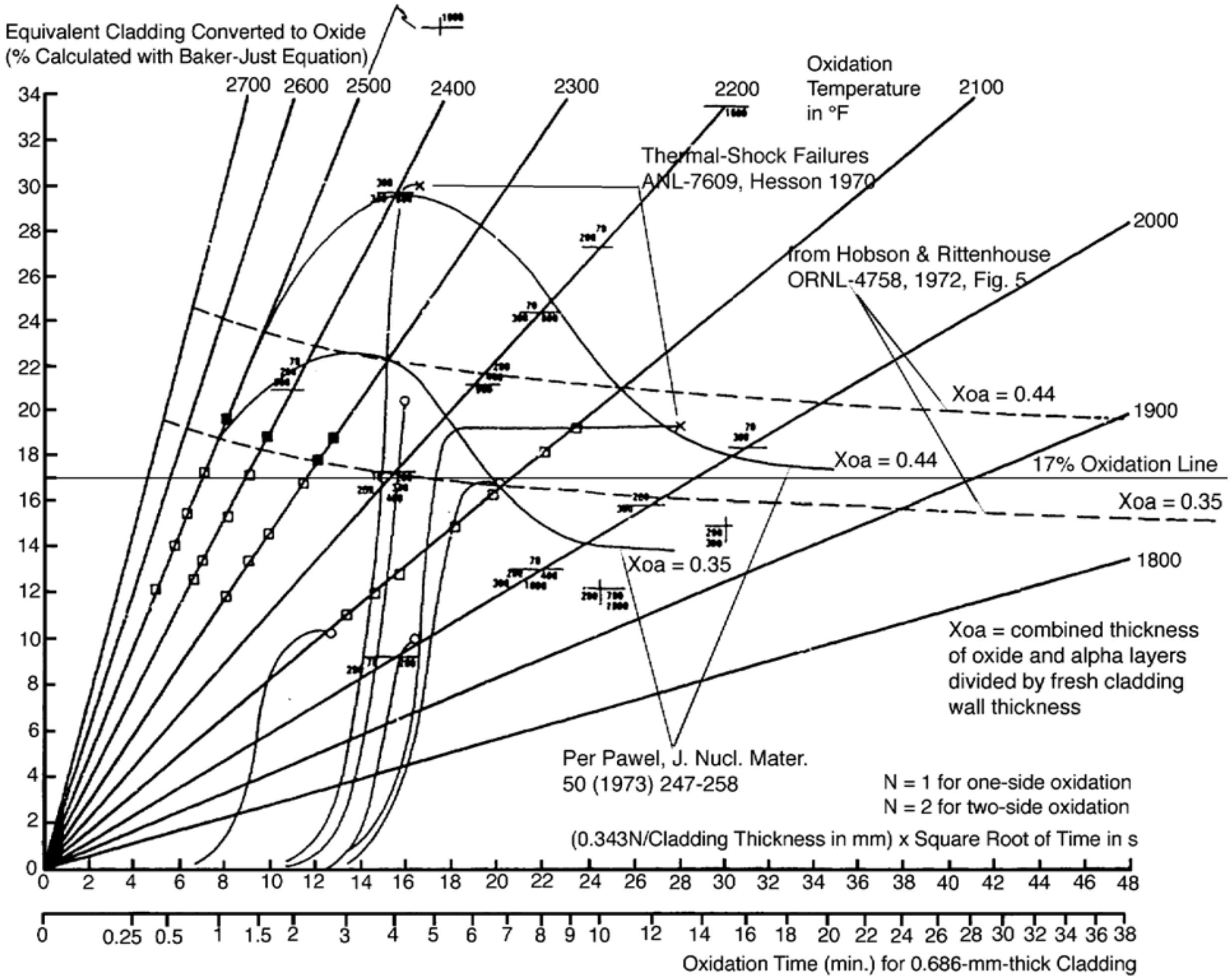


Figure 8.

Summary of multistep procedure used to establish 17% oxidation criterion during 1973 Rule-Making Hearing (from Docket RM-50-1, April 16, 1973). Note equivalent cladding oxidized was calculated per Baker-Just correlation. For comparison, time to reach threshold fraction of combined oxide and alpha layers of 0.44 is shown as determined per Hobson and Rittenhouse (ORNL-4758, January 1972) and Pawel (J. Nucl. Mater. 50, 1973, pp. 247-258).

By definition, **ECR parameter varies depending on cladding wall thickness,** either due to differences in fuel design or due to ballooning and burst during the heatup phase in a LOCA. Figure 8 shows how to take account of the effects of variations in wall thickness and one- vs. two-sided oxidation.

Two of Hesson's thermal-shock experiments resulted in cladding fragmentation at calculated ECR values of ≈19 and ≈30%, as indicated in the figure. The other four did not fail at ECR values of ≈21, ≈16.5, ≈10, and ≈9.5%. The time-temperature transients in Hesson's tests were integrated also by **using the Baker-Just equation**.

The CE data, discussed in the Hearing, are represented by squares on the oxidation isotherms of 2500, 2400, 2300, and 2100°F. If the sample fractured on compression by CE's load standard, it was considered to have failed and is denoted with a filled square. Open squares denote CE's non-failed specimens. By the CE's load standard, only those samples with calculated ECR values >17% failed.

Based on the results given in Fig. 7 and the five sets of information shown in Fig. 8, one can conclude that **no samples tested by slow compression at >135°C failed with zero ductility if equivalent cladding reacted (ECR), calculated on the basis of Baker-Just correlation, was less than 17%**. Furthermore, all samples oxidized to <17% ECR (again calculated with Baker-Just correlation) survived direct quenching.

In summary, the AEC Commissioners concluded that the very good consistency between the **17% limit, if calculated with the Baker-Just equation,** and a wide variety of experiments supports adoption of this procedure [21], and it was further stated:

> "There is relatively good agreement among the industrial participants as to what the limit on total oxidation should be.... The regulatory staff in their concluding statement compared various measures of oxidation and concluded that a 17 % total oxidation limit is satisfactory, **if calculated by the Baker-Just equation**... As argued by the regulatory staff, it appears that the 17% oxidation limit is within the Rittenhouse criteria. Thus a remarkable uniformity of opinion seems to exist with regard to the 17% oxidation limit [13]."

It is clear that the primary **rationale of the 17% criterion is retention of cladding ductility** at temperatures higher than 275°F (135°C, i.e., the saturation temperature during reflood). Of major importance in this proceeding is that the **threshold ECR value of 17% is tied with the use of Baker-Just correlation.** That is, the 17% ECR criterion is specific to Baker-Just correlation that must be used to determine the degree of total oxidation. If an oxidation correlation other than the Baker-Just equation (e.g., Cathcart-Pawel correlation) were used, the threshold ECR would have been less than 17%. This means that use of a best-estimate correlation may not necessarily be conservative in evaluating post-quench cladding ductility.

5.2 Other Embrittlement Criteria Proposed after the 1973 Hearing

Few months after the 1973 Hearing, Pawel proposed a new criterion based on <95 % saturation of the average oxygen concentration in the beta phase [27]. However, such a criterion fails to recognize that in addition to a sufficiently low O concentration, a minimum thickness of beta layer is required to ensure adequate resistance to failure. Such criterion is less facilitated to handle, especially during non-isothermal LOCA transients, and it requires a computer code that can accurately calculate O diffusion under moving-phase-boundary conditions, a task more difficult than the calculation of a simple parabolic oxidation correlation. Nevertheless, many of such computer codes have been developed after the 1973 Hearing, e.g., those reported in Refs. 17 and 24.

Sawatzky performed room-temperature tensile tests on specimens exposed to high-temperature spikes in steam [28]. Based on results of microhardness measurement, the distribution of O in the transformed beta (or prior beta) layer was found to be nonuniform, an observation confirmed subsequently by ANL investigators by Auger electron spectroscopy (Fig. 32-43, Ref. 17). In spite of total oxidation of only 16 %, a specimen with average O concentration >0.8 wt% in the prior beta exhibited very low strength and negligible elongation, whereas a specimen with O content <0.6 wt% in the prior beta retained some ductility. Based on this observation, Sawatzky proposed to replace the 1204°C PCT and the 17% ECR criteria by a unified criterion, that is, oxygen concentration in beta layer shall be <0.7 wt% over at least half of the cladding thickness. At temperatures >1280°C, Sawatzky's criterion is virtually identical to Pawel’s criterion (see Fig. 9).

Validity of the three criteria illustrated in Fig. 9 is, however, subject to variations in cladding wall thickness, because the time to reach the specified threshold state of material is strongly influenced by the clad wall thickness which may vary with fuel design and the degree of ballooning and burst. Thus, it was deemed desirable to develop a unified embrittlement criterion that would be valid independent of variations in wall thickness and oxidation temperature [17].

5.3 One- vs. Two-Side Oxidation and Thermal-Shock Failure

Grandjean et al. have reported results of extensive thermal-shock tests which were performed in TAGCIS facility [29,30]. Hydrogen uptake in their short ring specimens was not excessive. In their investigation, ECR was calculated with PECLOX oxidation code [31], and failure-survival behavior was determined based on the result of gas-leakage check. The results of the tests were included in Fig. 6. The effect of one- vs, two-side oxidation on thermal-shock failure was the focus of investigation. As indicated in Fig. 8, such effect was considered negligible in establishing the 17% ECR limit in the 1973 Rule-Making Hearing. Interestingly, Grandjean et al.'s failure threshold for two-side oxidation appears to be slightly higher than the threshold for one-sided oxidation, i.e., ≈21 vs. ≈20% ECR. Nonetheless, this study provides an independent confirmation of the validity of the 17% ECR criterion relative to susceptibility to thermal-shock failure.

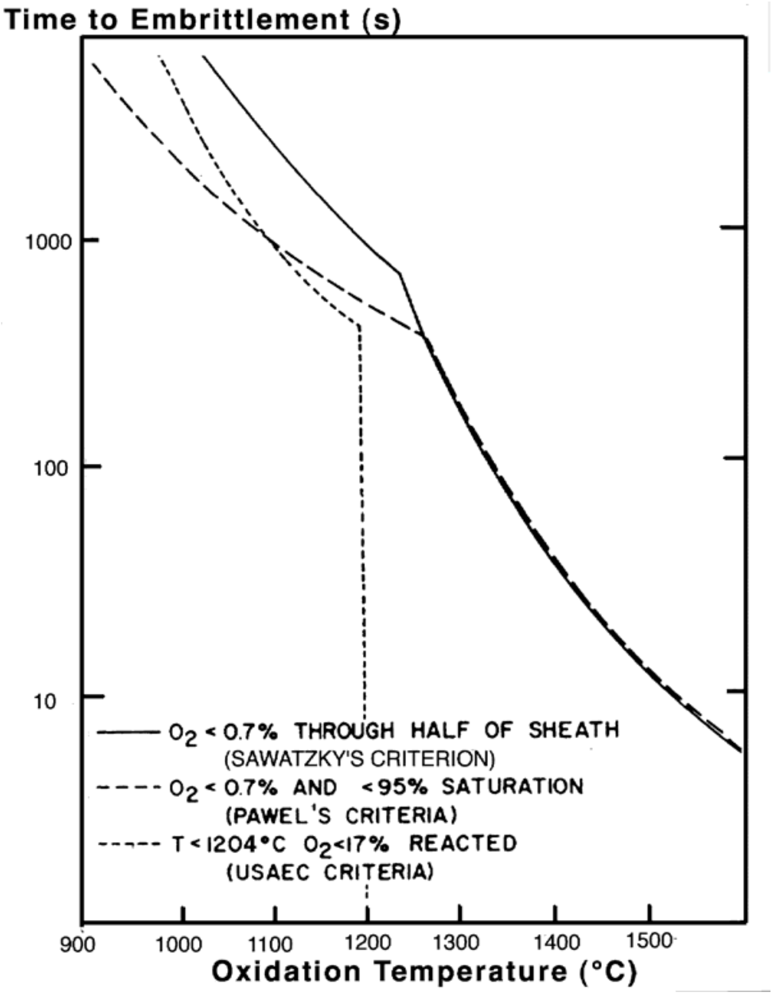


Figure 9.

Comparison of current embrittlement criteria with those proposed by Pawel (Ref. 27) and Sawatzky (Ref. 28).

5.4 <u>17% Oxidation Limit and Impact Failure at Small Hydrogen Uptake</u>

After the 1973 Hearing, ANL investigators conducted impact tests to provide an independent verification of the validity of 17% ECR threshold with respect to cladding resistance to impact failure [17]. Impact tests were performed at room temperature on non-pressurized open-ended Zircaloy-4 tubes that were oxidized on two sides in steam at 1100-1400°C and cooled through the beta-to-alpha-prime transformation range at 5 or ≈100°C/s. Because the sample was oxidized on both OD and ID sides, hydrogen uptake was limited to <130 wppm. Therefore, microstructure and oxygen and hydrogen distributions in the specimens were similar to those of the ring-compression specimens of Hobson [25,26] that were cooled fast through the beta-to-alpha-prime transformation range.

It was found that slow-cooled specimens were more resistant to impact failure than fast-cooled specimens (Fig. 65, Ref. 17]. Results obtained for slow-cooled specimens are summarized in Fig. 10. The ECR values in Fig. 10 were directly determined based on measured phase layer thickness, therefore, are considered more accurate than values calculated based on Baker-Just correlation. The results in Fig. 10 show that for cladding oxidized at <1315°C to <17% ECR, a sufficient level of resistance to impact failure is retained at 23°C, i.e., failure impact energy of >0.8 J.

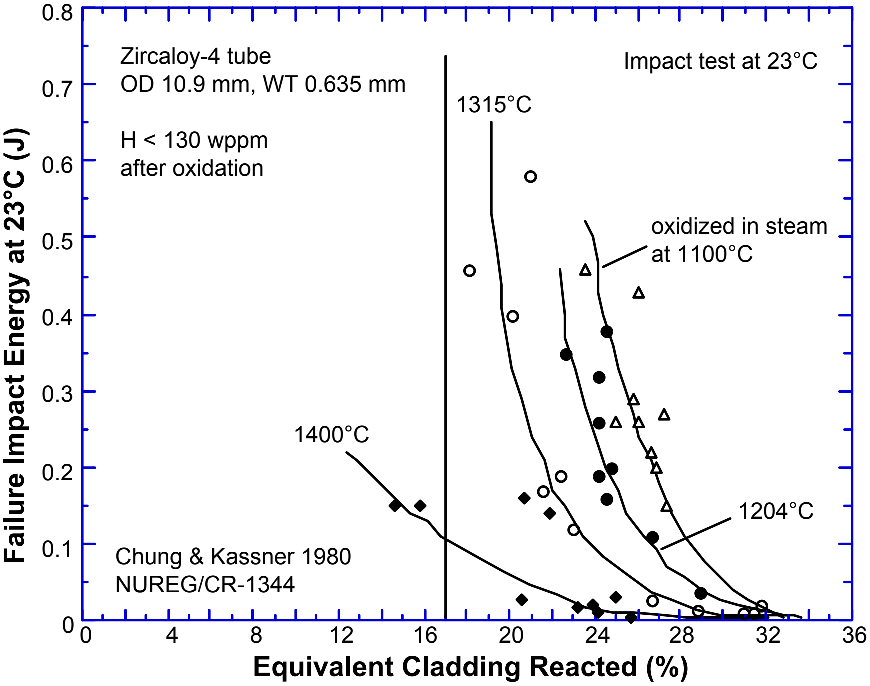


Figure 10.

Failure impact energy vs. equivalent cladding reacted, from tests at 23°C on undeformed Zircaloy-4 tube oxidized on two-sides and cooled at 5°C/s (Ref. 17).

5.5 <u>17% Limit and Ring-Compression Ductility at Small Hydrogen Uptake</u>

As shown in Fig. 8, the 17% threshold ECR was derived by indirect multistep procedure. Of particular importance in this procedure is the accuracy of two key factors, i.e., (1) temperature measurement in the experiments of Baker-Just and Hobson-Rittenhouse [25,26] and (2) definition of nil-ductility as given in Fig. 7. In consideration of this, ANL investigators performed independent compression tests at room temperature on short Zircaloy-4 ring specimens. Rings were sectioned from long tubes that were oxidized in steam at 1100-1400°C and cooled through the beta-to-alpha-prime transformation range at 5 or ≈100°C/s. Hydrogen uptake in the ring specimens was <130 wppm. This procedure reproduced the conditions of the ring-compression tests of Hobson. In the ANL compression tests, however, load-deflection curves were obtained to better quantify the degree of remaining ductility and the magnitude of load that a ring can sustain.

It was found that slow-cooled specimens retained more ductility than fast-cooled specimens under otherwise identical conditions (Fig. 67, Ref. 17]. Figure 11 summarizes results obtained for a slow-cooling rate of ≈5°C/s, a rate probably more prototypic of a LOCA than fast cooling. The ECR values in the figure were determined based on measured phase layer thickness and time-temperature history. This result shows that for cladding oxidized at <1315°C to <17% ECR, ductility is retained at 23°C (i.e., relative diametral deflection >16%); no brittle failure was observed. This experiment provides an independent confirmation of the validity of the 17% oxidation limit for undeformed Zircaloy specimens that contain hydrogen <130 wppm.

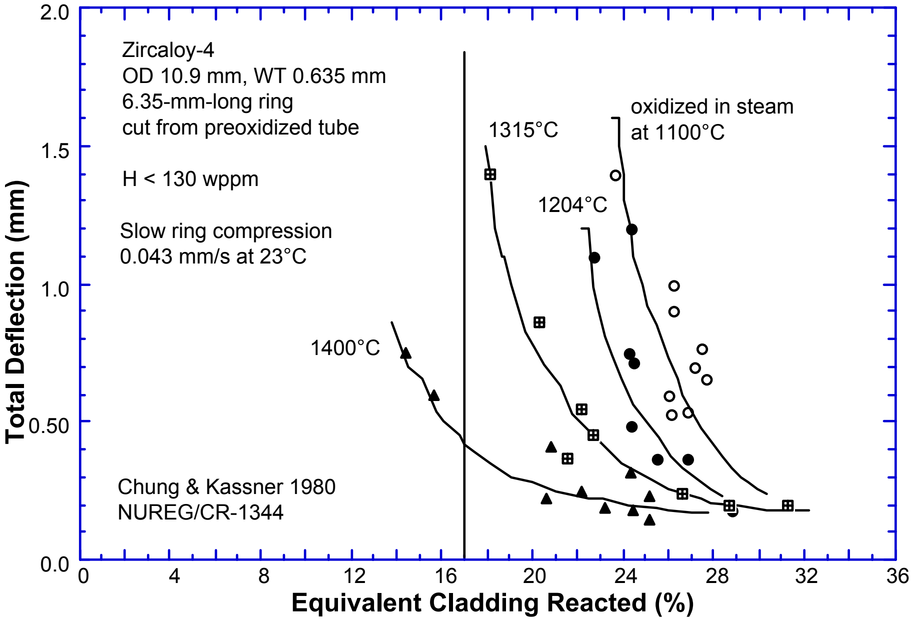


Figure 11.

Total deflection at 23°C vs. equivalent cladding reacted, from ring-compression tests on Zircaloy-4 oxidized on two-sides and cooled at 5°C/s (Ref. 17).

5.6 Resistance to Impact Failure at Large Hydrogen Uptake

In addition to the impact tests on non-ruptured empty tubes, ANL investigators performed 0.15- and 0.3-J pendulum impact tests at 23°C on pressurized Zircaloy-4 tubes that were burst, oxidized, cooled at ≈5°C/s, and survived quenching thermal shock [17]. The CSNI experts [18] considered that: "Ambient impact of 0.3 J were thought to be a reasonable approximation to post LOCA quench ambient impact loads." The results of the 0.3-J impact tests, summarized in Fig. 12, indicate that the 17%-ECR limit is adequate to prevent a burst-and-oxidized cladding from failure under 0.3-J impact at 23°C, as long as peak cladding temperature remained ≤1204°C. The ECR values in the figure were determined based on measured thickness of oxide, alpha, and beta phase layers, rather than calculated based on Baker-Just correlation, and hence, are considered more accurate.

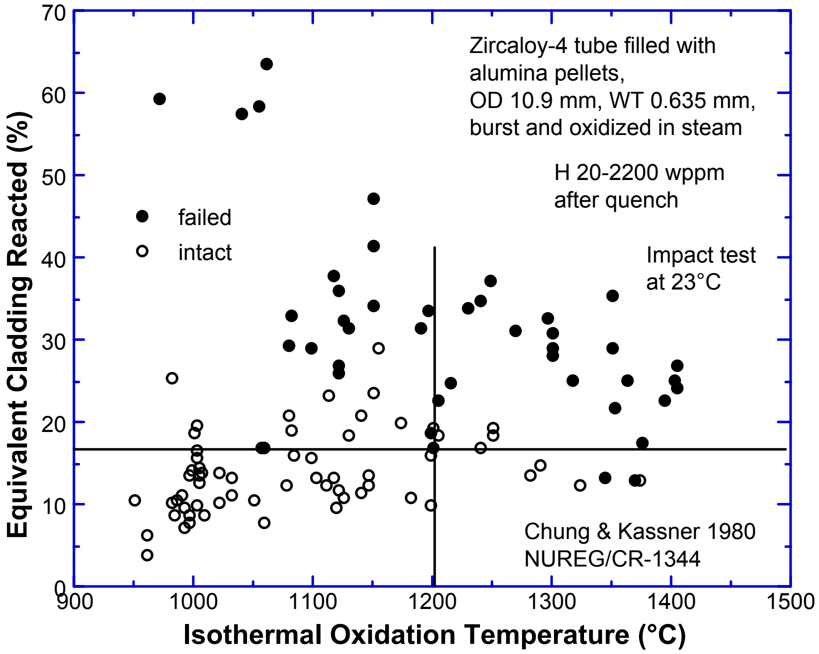


Figure 12.

Impact failure threshold as function of equivalent cladding reacted and oxidation temperature of burst, oxidized, slow-cooled, and quenched Zircaloy-4 tube containing 20-2200 wppm hydrogen (from Ref. 17).

In contrast to two-side-oxidized non-pressurized non-ruptured tubes in which hydrogen uptake was small (<130 wppm), burst Zircaloy-4 tubes exhibited peculiar oxidation behavior near the burst opening. The inner-diameter (ID) surfaces of the top and bottom "necks," ≈30-mm away from the burst center, were exposed to hydrogen-rich stagnant steam-hydrogen mixture which is produced because of poor mixing of steam and hydrogen at the narrow gap between the alumina pellets and the ID surface of the necks. As a consequence, thick breakaway oxides formed at 900-1120°C [17], and hydrogen uptake as high as ≈2200 wppm was observed at the "necked" regions. Subsequently, JAERI investigators confirmed occurrence of the same phenomenon [32,33].

The results from the same tests shown in Fig. 12 were converted to failure-survival map based on average hydrogen content of the impact-loaded local region and the thickness of transformed-beta layer containing <0.7 wt.% oxygen. This failure-survival map is shown in Fig. 13. On the basis of the figure, ANL investigators proposed to replace the 1204°C PCT and 17% ECR criteria by a unified criterion which specifies that the thickness of transformed-beta layer containing <0.7 wt.% oxygen shall be >0.3 mm [17]. The criterion implicitly incorporates a limit in peak cladding temperature. This limiting temperature corresponds to the temperature at which oxygen solubility is 0.7 wt.% in Zircaloy that contains 700-1200 wppm hydrogen. This temperature is believed to be between 1200 and 1250°C, although the exact data from applicable Zircaloy-O-H ternary diagrams are not. This criterion is not subject to variations in cladding wall thickness and oxidation temperature.

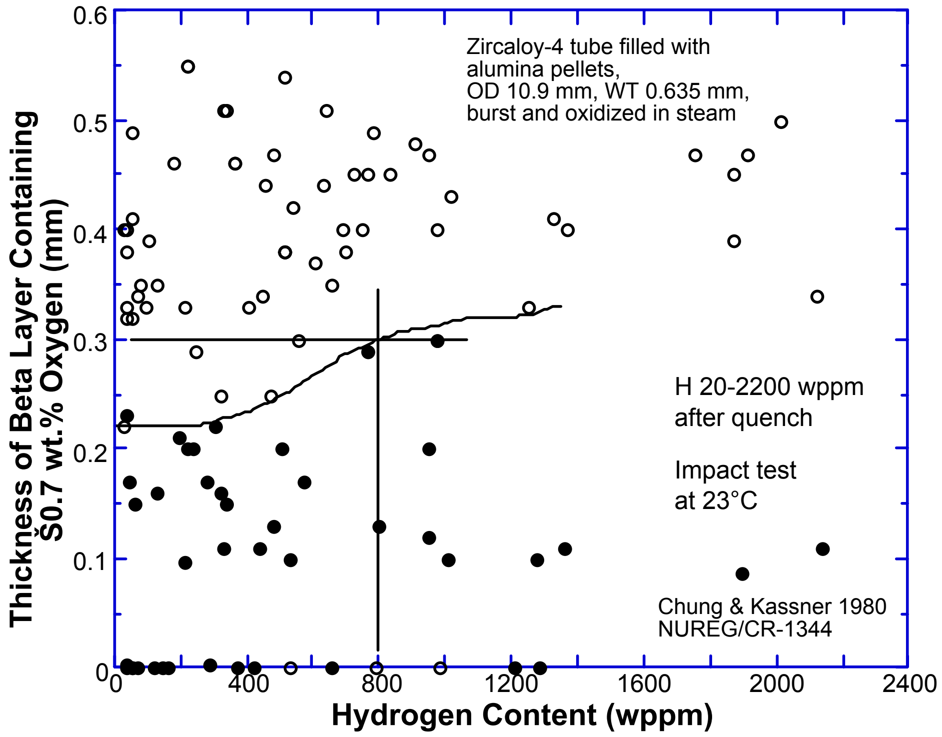


Figure 13.

Impact failure map as function of hydrogen content and thickness of beta layer containing ≤0.7 wt.% oxygen; Zircaloy-4 tube burst, oxidized, slow-cooled, and quenched (from Ref. 17).

The results in Fig. 13 show that for a given thickness and a given oxygen content in transformed-beta layer, resistance of cladding to impact failure is significantly reduced if hydrogen uptake exceeds ≈700 wppm. Such situation does not occur in non-pressurized, non-ruptured, two-side-oxidized Zircaloy cladding, such as those tested by Hobson [26] or discussed in Figs. 10 or 11.

5.7 Ring-Compression Ductility at Large Hydrogen Uptake

Investigators in ANL [17] and JAERI [32,33] conducted extensive tests on tube or ring specimens of Zircaloy-4 that contained high concentrations of hydrogen. In the former investigation, Zircaloy-4 tubes filled with alumina "pellets" were pressurized, heated, burst, oxidized, slow-cooled, and quenched with bottom-flooding water. Then, the tubes that survived the quenching thermal shock were compressed diametrically at 23°C [17]. Such specimens contained H up to ≈2200 wppm. In the latter investigation, short rings, sectioned from tubes that were exposed to similar conditions, were compressed at 100°C. The ring specimens contained H up to ≈1800 wppm. Typical distributions of oxide layer thickness, hydrogen concentration, and ring deflection to failure are shown in Fig. 14. The top and bottom "necks" that contained the highest concentration of hydrogen and the thinnest transformed-beta layer exhibited the lowest ductility.

However, ANL investigators observed that the rate of hydrogen generation, amount of hydrogen uptake, and hence, the degree of embrittlement of the necked regions are strongly influenced by the method of heating cladding tubes during LOCA-like transients, i.e., more uniform (indirect heating in JAERI) vs.

less uniform (direct heating in ANL) heating [17]. This is schematically illustrated in Fig. 15.

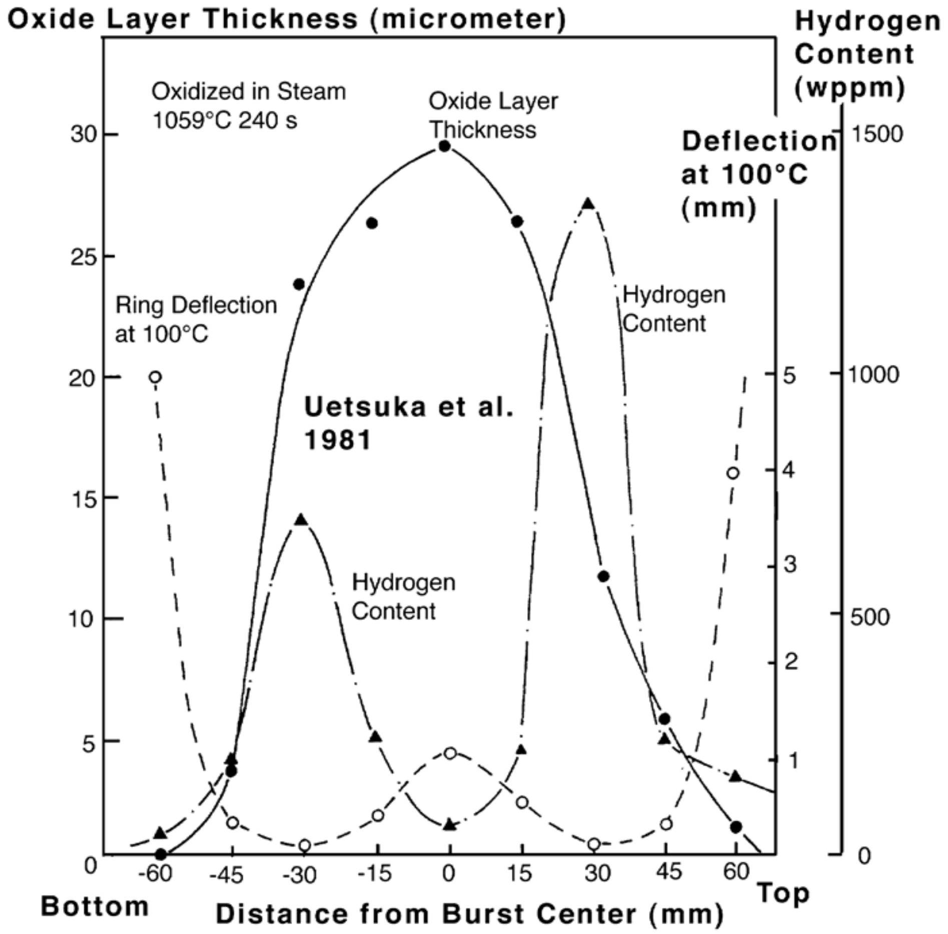
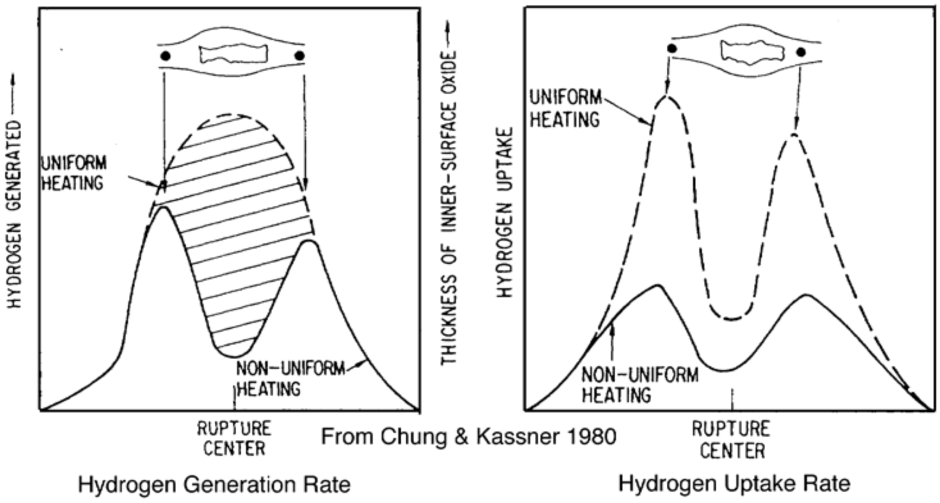


Figure 14.

Distributions of hydrogen content, inner-diameter oxide layer thickness, and total deflection at 100°C of ring specimens sectioned from burst region (from Uetsuka et al., Refs. 32 and 33).

The effect of hydrogen uptake on post-quench ductility, determined either from diametral-compression test of burst-and-oxidized tubes at 23°C [17] or compression at 100°C of ring specimens sectioned from burst-and-oxidized tubes [32,33], is summarized in Fig. 16. At hydrogen uptake >700 wppm, significant embrittlement of cladding is evident, even if total oxidation is <17% (see Fig. 14). Similar dependencies of plastic deflection on beta-layer oxygen content and total hydrogen content have been also reported in Fig. 88, Ref. 17 and Fig. 89, Ref. 17, respectively. These results show that post-quench ductility of Zircaloy is strongly influenced by not only oxidation but also hydrogen uptake. This is shown in Fig. 17. Apparently, the important effect of hydrogen uptake on post-quench ductility was not well realized at the time of 1973 Hearing.



From Chung & Kassner 1980

Hydrogen Generation Rate

Hydrogen Uptake Rate

Figure 15.

Effect of heating method (uniform vs. nonuniform heating) on hydrogen generation and uptake near burst opening (from Ref. 17)

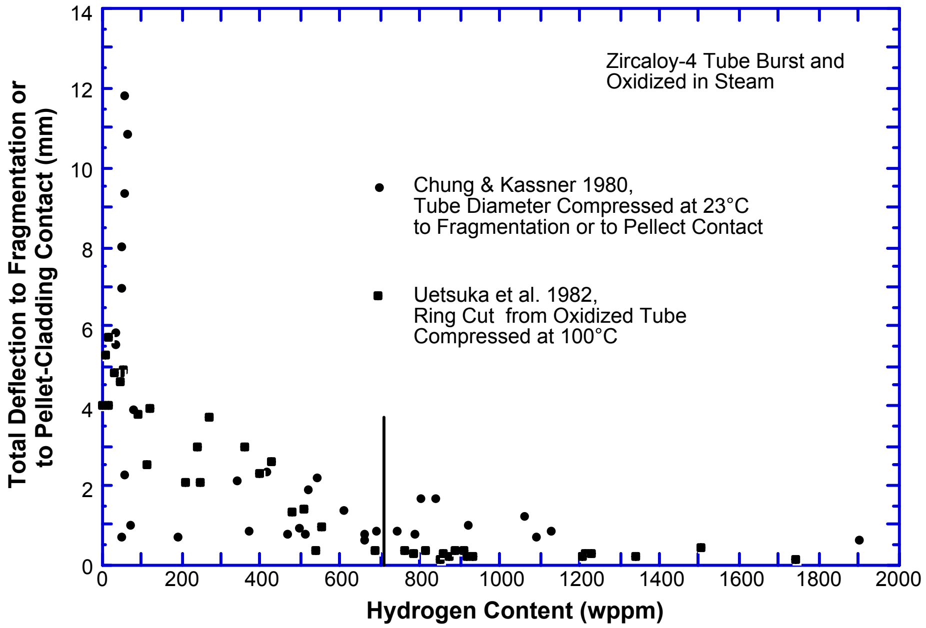


Figure 16.

Effect of hydrogen uptake on diametral deflection of burst, oxidized, and quenched Zircaloy-4 tube or sectioned ring.

Essentially similar observation has also been reported by Komatsu et al. [34,35]. They reported that the load to initial ring cracking is strongly influenced by total oxidation and hydrogen uptake. For oxidation temperatures >1260°C in which the oxygen content in the beta layer exceeds ≈0.7 wt.% in short period of time, the embrittling effect of oxygen appears to be predominant (see Fig. 18). The "zero-ductility" region denoted in Fig. 18 appears to have been determined based on a threshold load to initial cracking rather than based on ductility consideration. As such, this "zero-ductility" threshold differs significantly from that defined by Hobson [25,26].

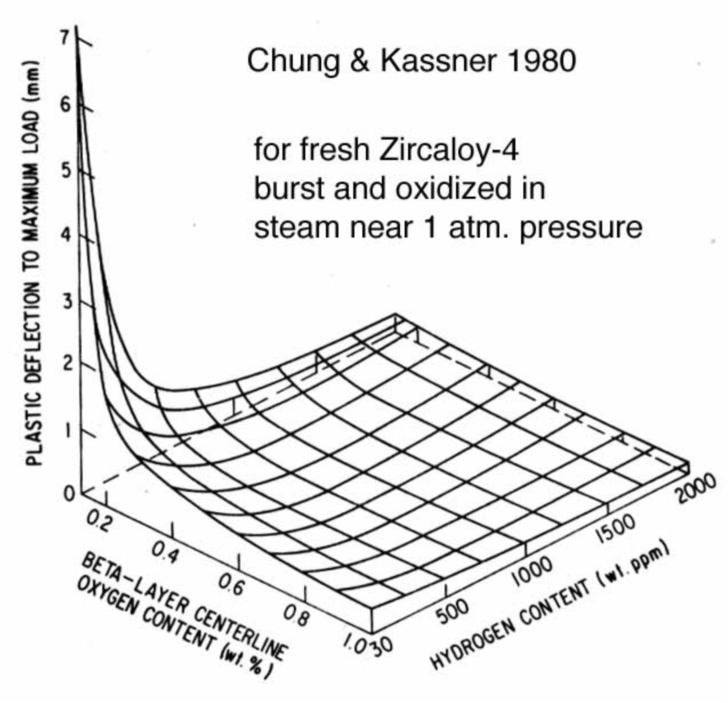


Figure 17.

Post-quench ductility shown as function of oxidation (beta-layer centerline oxygen content) and total hydrogen content, from diametral compression test at 23°C on burst, oxidized, slow-cooled, and quenched Zircaloy-4 tubes (for database see Ref. 17).

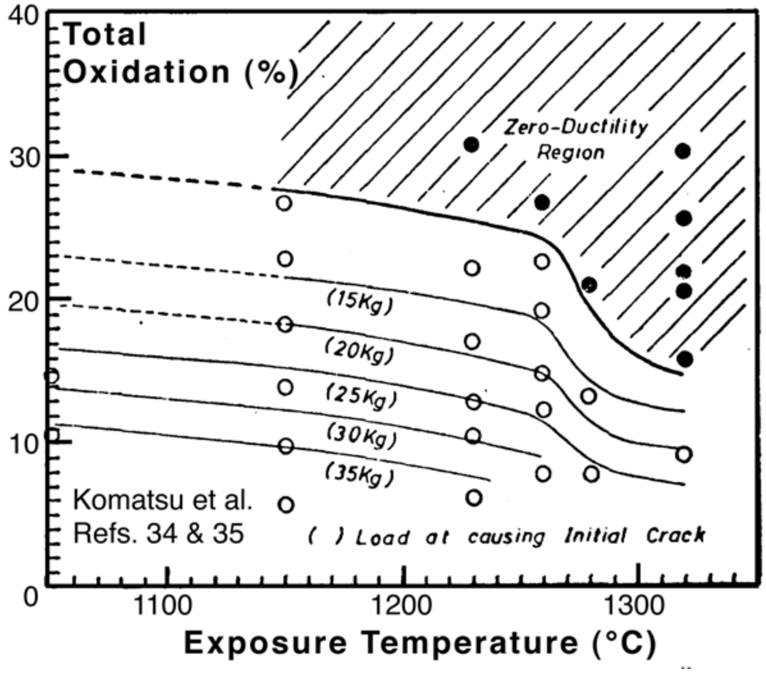


Figure 18.

Applied load at initial cracking of ring as function of total oxidation and exposure temperature, from Komatsu et al., Refs. 34 and 35.

5.8 <u>17% Oxidation Criterion - Summary</u>

It is clear that the primary rationale of the 17% ECR criterion is retention of cladding ductility at temperatures higher than 275°F (135°C), i.e., the saturation temperature during reflood. The threshold ECR value of 17% is tied with the use of Baker-Just correlation. If a best-estimate correlation other than

Baker-Just equation (e.g., Cathcart-Pawel correlation) were used, the threshold ECR would have been <17%.

Investigations conducted after the 1973 Rule-Making Hearing showed that for oxidation temperatures ≤1204°C, the 17% oxidation limit (as calculated with Baker-Just correlation) is adequate to ensure survival of fully constrained or unconstrained cladding under quenching thermal shock. It was also shown that the 17% limit (ECR determined on the basis of measured phase layer thickness) is adequate to ensure retention of ductility and resistance to 0.3-J impact failure in non-irradiated, non-ruptured, two-side-oxidized Zircaloy cladding in which hydrogen uptake during a LOCA-like transient is small.

However, the 17% limit appears to be inadequate to ensure post-quench ductility for hydrogen uptake >700 wppm. Such level of large hydrogen uptake could occur in some types of fuel rods during normal operation, especially at high burnup, or during a LOCA-like transient in localized regions in a ballooned and ruptured node.

6. 1204°C (2200°F) Peak Cladding Temperature Criterion

6.1 Selection of 1204°C Criterion in 1973 Hearing

From the results of posttest metallographic analysis of the slow-ring-compression specimens, Hobson [26] observed a good correlation between zero ductility temperature (ZDT) and fractional thickness of transformed-beta layer (or the sum of oxide plus alpha layer thickness) as long as the specimen was oxidized at ≤2200°F (1204°C) (see Fig. 7). However, in spite of comparable thickness of transformed beta layer, specimens oxidized at 2400°F (1315°C) were far more brittle. This observation was explained on the basis of excessive solid-solution hardening of transformed-beta phase at high oxygen concentrations. For mechanical properties near room temperature the critical concentration of oxygen in the transformed-beta was estimated to be ≈0.7 wt%. Above this concentration, transformed beta phase becomes brittle near room temperature. Because of the solubility limit of oxygen in the beta phase, this high O concentration cannot be reached at 2200°F (1204°C) but can be reached at 2400°F (1315°C). Hobson concluded that: "embrittlement is not simply a function of the extent of oxidation alone, but is related in yet another way to the exposure temperature."

During the 1973 Rule-Making Hearing, AEC Staff endorsed Hobson's conclusion and wrote: "The staff recognizes the importance of oxygen concentration in the beta phase in determining the load bearing ability of Zircaloy cladding, and the implication from the recent compression tests that this may not be satisfactorily characterized above 2200°F by a ZDT as a function of remaining beta fraction only. We therefore believe that **peak cladding temperatures should be limited to 2200°F** [20]."

Subsequently, it was also concluded that:

"Additional metallurgical and slow compression mechanical tests on other quenched samples from the ORNL experiments indicated that an important consideration was the amount and distribution of oxygen in the nominally ductile prior-beta phase. However, these factors could not be correlated as functions of time and temperature in the same manner as the (combined oxide and alpha layer) penetration. In particular, the slow compression tests indicated a greater degradation in cladding ductility at higher temperatures than would be expected from considerations of (combined oxide and alpha layer) penetration alone. It was on this basis that **the staff previously suggested a 2200°F maximum cladding temperature**... What was observed in the slow compression tests was that 6 samples exposed at 2400°F for only two minutes and with relatively high values of Fw (Fw being fractional thickness of prior beta, all greater than 0.65) all fractured with nil ductility... Only when brittle failure was detected at high Fw in the slow compression tests did the suspicion arise that ductility was a function of both Fw and the exposure temperature... As the temperature rises above 2200-2300°F, solid solution hardening in the beta phase appears to contribute significantly to formation of a brittle structure. That is, brittle failure occurs even though alpha incursions are not observed, and the fraction of remaining beta is greater than that observed in lower temperature tests. This is confirmed by examination of the six samples from the ORNL exposed at 2400°F for two minutes (Exhibit 1126)... From the foregoing, there is ample evidence that load bearing ability and ductility decrease with increasing exposure temperatures, even for transients with comparable Fw. Increased solubility of oxygen in the prior-beta phase has been discussed as a contributing factor... The staff believes that because of high temperature degradation ... phenomena (... strongly suggested by the experimental evidence cited), **the suggested 2200°F limit should be imposed** [21]."

Then it was added:

"The situation is complicated by the fact that not all of the prior beta phase is equally strong or ductile, since these properties depend on the amount of dissolved oxygen. This fact has been suspected for some time... From the phase diagram, given by both Scatena and Westinghouse, it is obvious that it is possible for the beta phase zirconium to take on a higher oxygen content at 2600°F than at 2000°F. Furthermore, since the diffusion rate depends exponentially upon temperature, one might expect a greater incursion of oxygen into the beta phase for a given thickness of oxide and stabilized alpha phase at higher temperatures... Others (than Hobson) have also observed that the resistance to rupture depends upon the temperature at which oxidation occurs as well as the extent of oxidation... To recapitulate, measures of Zircaloy oxidation, whether by percent, X_T, or F_W, are largely or wholly determined from the brittle layers of zirconium oxide or stabilized alpha phase, while the ductility and strength of oxidized zirconium depend upon the condition and the thickness of the prior beta phase... Thus a criterion based **solely on the extent of total oxidation is not enough, and some additional criterion is needed** to assure that the prior beta phase is not too brittle. The specification of a maximum temperature of 2200°F will accomplish this **adequately. The data cited in exhibit 1113 would not support a choice of a less conservative limit** [13]."

Few months after the Hearing, Pawel [27] explained Hobson's observation based on data that indicate oxygen solubility in the beta Zr at 2200-2400°F (1204-1316°C) is ≈0.7 wt.%. The O solubility in beta Zircaloy is significantly influenced by not only temperature but also the concentration of hydrogen, a strong beta stabilizer. Nevertheless, Pawel endorsed that: "...the above reasoning easily explains why the mechanical or load bearing properties of the oxidized specimens should not be a unique function of the extent of (total) oxidation." Consequently, Pawel proposed to replace the peak cladding temperature (PCT) criterion by a new criterion that specifies the average oxygen concentration in the beta phase shall be less than 0.7 wt% [see Fig. 9].

6.2 1204°C Limit vs. In-Pile Test Results

In 1970s, high-temperature oxidation and embrittlement behaviors were investigated extensively in TREAT and PBF test reactors. During the TREAT-FRF2 test, a seven-rod cluster was oxidized at 2400°F (≈1315°C) [36]. According to hardness measurements, all rods contained portions that possessed no ductility at room temperature. Three rods were broken accidentally during handling in ORNL hot cell, which indicates the degree of brittleness of a badly embrittled rod and the magnitude of a typical load during handling in hot cell (see Fig. 19).

Some fuel rods tested in the Power Burst Facility (PBF) were also known to have failed during handling or posttest examination in hot cell. This information is summarized in Fig. 20 [37]. Total oxidation of several failed rods were <17 %. Of particular interest is Rod IE-019 of Test IE 5, because ballooning and burst occurred in the rod before exposure to temperatures >1100°C. In spite of the fact that ECR was only ≈12%, the rod broke into pieces after exposure to an "equivalent" oxidation temperature of ≈1262°C. Most likely, actual peak temperature was higher than this equivalent temperature. Rod A-0021 also ruptured before entering high temperature transient; this caused ingress of steam to the rod interior. The rod failed after exposure to ≈1307°C, although ECR was only ≈6%. Hydrogen uptake in the two rods was excessive because of exposure to stagnant steam near the rupture opening.

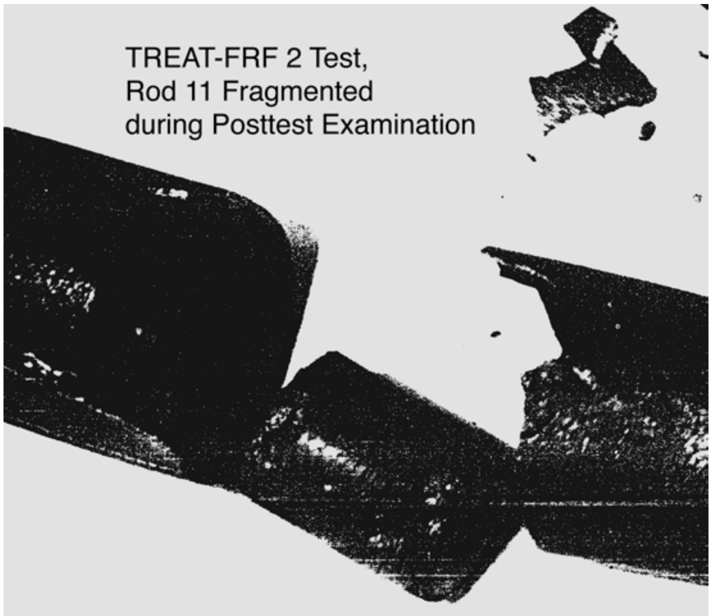


Figure 19.

Fuel pellet released through fragmented cladding section of Rod 11, TREAT-FRF 2 Test (from Ref. 37).

It is not clear if the failure behavior of Rods IE-019 and A-0021 is predicted based on Pawel's criterion (Fig. 9). However, because the exposure temperatures of the rods exceeded ≈1262°C, the thickness of beta layer that contained ≤0.7 wt.% oxygen should have been zero or close to zero. However, because oxygen solubility in beta is influenced by hydrogen and because accurate peak temperatures reached in the rods are not well known, it is difficult to calculate accurately the thickness of beta layer that contains O ≤0.7 wt.%. Therefore, it is not clear if the failure behavior of the two rods is consistent with the criterion shown in Fig. 13.

As long as clad oxidation temperature was limited to ≤1204°C, a handling failure at measured ECR <17% was not observed from the TREAT and PBF tests or the ANL 0.3-J impact tests (see Fig. 20). This observation clearly demonstrates the importance of the 1204°C PCT limit. That is, the 1204°C PCT and the 17% ECR limits are inseparable, and as such, constitute an integral criterion.

6.3 Summary of 1204°C Criterion

The 2200°F (1204°C) peak cladding temperature (PCT) criterion was selected on the basis of Hobson's slow-ring-compression tests that were performed at 25-150°C. Samples oxidized at 2400°F (1315°C) were far more brittle than samples oxidized at <2200°F (<1204°C) in spite of comparable level of total oxidation. This is because oxygen solid-solution hardening of the prior-beta phase is excessive at oxygen concentrations >0.7 wt%.

The selection of the 1204°C criterion was subsequently justified by the observations from the ANL 0.3-J impact tests and the handling failure of rods tested in the Power Burst Facility. These results also take into account of the effect of large hydrogen uptake that occurred near the burst opening. Consideration of potential for runaway oxidation alone would have lead to a PCT limit somewhat higher than 2200°F (1204°C). In conjunction with the 17% oxidation criterion, the primary objective of the PCT criterion is to ensure adequate margin of protection against post-quench failure that may occur under hydraulic, impact, handling, and seismic loading.

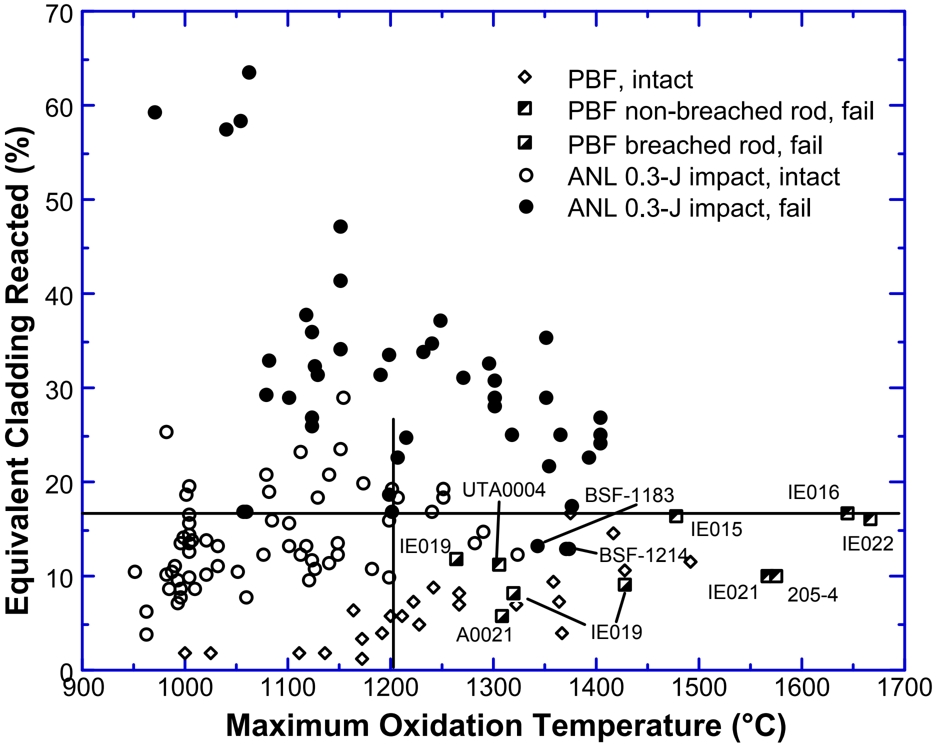


Figure 20.

Comparison of data from hot-cell handling failure of Zircaloy rods exposed to high temperature in Power Burst Facility (Ref. 37) and 0.3-J impact tests in ANL (Ref. 17).

7. Conclusions

1. In the 1973 Rule-Making Hearing, the U. S. Atomic Energy Commission (AEC) staff and commissioners were clearly reluctant to neglect the effect of mechanical constraints on the susceptibility of oxidized fuel cladding to thermal-shock fragmentation. Subsequent test results appear to justify this rationale. Results from unconstrained or partially constrained quench tests were considered only corroborative; their use for regulatory purposes was not accepted.

2. The AEC staff and commissioners and OECD-CSNI specialists were of the opinion that retention of ductility was the best guarantee against potential fragmentation of fuel cladding under various types of not-so-well-quantified loading, such as thermal shock, hydraulic, and seismic forces, and the forces related with handling and transportation.

3. Primary rationale of the 17% oxidation criterion was retention of cladding ductility at temperatures higher than 275°F (135°C), i.e., the saturation

temperature during reflood. The threshold equivalent cladding reacted (ECR) of 17% is tied with the use of Baker-Just correlation. If a best-estimate correlation other than Baker-Just equation (e.g., Cathcart-Pawel correlation) had been used, the threshold ECR would have been <17%.

4. Investigations conducted after the 1973 Rule-Making Hearing show that for oxidation temperatures ≤1204°C, the 17% oxidation limit (calculated with Baker-Just correlation) is adequate to ensure survival of unconstrained or fully constrained cladding under quenching thermal shock. It was also shown that the 17% limit (ECR determined on the basis of measured phase layer thickness) is adequate to ensure retention of ductility and resistance to 0.3-J impact failure in non-irradiated non-ruptured two-side-oxidized Zircaloy cladding in which hydrogen uptake during a LOCA-like transient is small.

5. However, the 17% ECR limit appears to be inadequate to ensure post-quench ductility at hydrogen concentrations >700 wppm. A major finding from tests performed after the 1973 Rule-Making Hearing shows that post-quench ductility is strongly influenced by not only oxidation but also hydrogen uptake. It seems that this effect of large hydrogen uptake was not known at the time of 1973 Hearing.

6. By definition, an embrittlement criterion expressed in terms of ECR is subject to uncertainties because calculated ECR varies with variations in cladding wall thickness and the degree of ballooning.

7. The 1204°C peak cladding temperature (PCT) limit was selected on the basis of slow-ring-compression tests that were performed at 25-150°C. Samples oxidized at 1315°C were far more brittle than samples oxidized at 1204°C in spite of comparable level of total oxidation. This is because oxygen solid-solution hardening of the prior-beta phase is excessive at oxygen concentrations >0.7wt%. Consideration of potential for runaway oxidation was a secondary factor in selecting the 1204°C limit. The 1204°C limit was subsequently justified by the observations from impact tests and handling failure of fuel rods exposed to high temperatures in the Power Burst Facility. The 1204°C PCT and the 17% ECR limits are inseparable, and as such, constitute an integral criterion.

8. The degree of oxygen saturation and the thickness of beta layer that contains oxygen concentrations ≤0.7 wt.% were important parameters used by investigators to develop new embrittlement criteria based on beta phase thickness rather than total oxidation. Such a criterion is not subject to inherent uncertainties associated with variations in cladding wall thickness and pre-LOCA oxidation.

9. Post-quench ductility and toughness are determined primarily by the thickness and the mechanical properties of transformed-beta layer. The mechanical properties are strongly influenced by several factors such as:

oxygen solubility in beta, concentrations of alpha- (tin and oxygen) and beta-stabilizing elements (niobium and hydrogen), the nature of beta-to-alpha-prime transformation, redistribution of oxygen, niobium, and hydrogen during the transformation, and precipitation of hydrides. Significantly large hydrogen uptake can occur in some types of fuel cladding, during normal operation to high burnup, during breakaway oxidation at <1120°C, and, for localized regions near a rupture opening, during LOCA transients. Hydrogen uptake and its effect on the properties of transformed beta could differ significantly in Zircaloys and in niobium-containing alloys. Considering these factors, it is recommended to obtain a better understanding of the effects of more realistic hydrogen uptake and niobium addition on the properties of transformed-beta layer and post-quench ductility.

Acknowledgments

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References

1. Grandjean, C. et al., "Oxidation and quenching experiments with high burnup cladding under LOCA conditions," Proc. 26th Water Reactor Safety Information Meeting, Bethesda, USA, 26-28 October, 1998.
2. Mardon, J.P. et al., "The M5 fuel rod cladding," Proc. ENS TOP'FUEL 99, Avignon, France, 13-15 September, 1999.
3. Nagase, F. et al., "Experiments on high burnup fuel behavior under LOCA conditions at JAERI," Proc. ANS Topical Meeting on LWR fuel Performance, Park City, USA, 10-13 April, 2000.
4. Ozawa, M. et al., "Behavior of irradiated zircaloy4 fuel cladding under simulated LOCA conditions," Proc. 12th Symp. on Zirconium in the Nuclear Industry, Toronto, Canada, 15-18 June, 1998.
5. Aomi, M. et al., "Behavior of irradiated BWR fuel cladding tubes under simulated LOCA conditions," Proc. ANS Topical Meeting on LWR fuel Performance, Park City, USA, 10-13 April, 2000.
6. Chung, H.M. et al., "Test plan for high-burnup fuel cladding behavior under loss-of-coolant accident conditions," Proc. 24th Water Reactor Safety Information Meeting, Bethesda, USA, 21-23 October, 1996.
7. Report of Advisory Task Force on Power Reactor Emergency Cooling, TID-24226, 1967.
8. General Design Criteria for Nuclear Power Plants, U.S. Code of Federal Regulations, Title 10, Part 50, Appendix A, 20 February, 1971, amended.
9. Interim Acceptance Criteria for Emergency Core-Cooling Systems for Light-Water Power Reactors, U.S. Federal Register 36 (125), pp. 12247-12250, 29 June, 1971.

10. Cottrell, W.B., "ECCS rule-making hearing," Nucl. Safety 15 (1974) 30-55.
11. New acceptance criteria for emergency core-cooling systems of light-water-cooled nuclear power reactors, Nucl. Safety 15 (1974) 173-184.
12. Acceptance Criteria for Emergency Core Cooling Systems for Light-Water Nuclear Power Reactors, U.S. Code of Federal Regulations, Title 10, Part 50, Section 46, 4 January, 1974, Amended.
13 Atomic Energy Commission Rule-Making Hearing, Opinion of the Commission, Docket RM-50-1, 28 December, 1973.
14. Hesson, J.C. et al., Laboratory Simulations of Cladding-Steam Reactions Following Loss-of-Coolant Accidents in Water-Cooled Power Reactors, ANL-7609, January 1970.
15. Parker, G.W. et al., "Release of fission products from reactor fuels during transient accidents simulated in TREAT," Proc. Intl. Symp. Fission Product Release and Transport under Accident Conditions, Oak Ridge, USA, 5-7 April, 1965.
16. Fujishiro, T. et al., "Light water reactor fuel response during reactivity initiated accident experiments," NUREG/CR-0269, August 1978.
17. Chung, H.M. and Kassner, T.F., Embrittlement Criteria for Zircaloy Fuel Cladding Applicable to Accident Situations in Light-Water Reactors, NUREG/CR-1344, January 1980.
18. Parsons, P.D. et al., The Deformation, Oxidation and Embrittlement of PWR Fuel Cladding in a Loss-of-Coolant Accident: A State-of-the-Art Report, CSNI Report 129, December 1986.
19. Zuzek, E. et al., "The H-Zr (hydrogen-zirconium) system," Bulletin of Alloy Phase Diagrams, 11 (1990) 385-395.
20. Atomic Energy Commission Rule-Making Hearing, Supplemental Testimony of the Regulatory Staff Docket RM-50-1, 26 October, 1972.
21. Atomic Energy Commission Rule-Making Hearing, Concluding Statement of the Regulatory Staff, Docket RM-50-1, 16 April, 1973.
22. Uetsuka, H. et al., "Failure-bearing capability of oxidized Zircaloy-4 cladding under simulated loss-of-coolant condition," J. Nucl. Sci. Tech. 20 (1983) 941-950.
23. Reocreux, M. and Scott de Martinville, E., "A study of fuel behavior in PWR design basis accident: An analysis of results from the PHEBUS and EDGAR experiments," Nucl. Eng. Design 124 (1990) 363-378.
24. Suzuki, M. and Kawasaki, S., "Development of computer code PRECIP-II for calculation of Zr-steam reaction," J. Nucl. Sci. Tech. 17 (1980) 291.
25. Hobson, D.O., and Rittenhouse, P. L., "Embrittlement of Zircaloy Clad Fuel Rods by Steam During LOCA Transients," ORNL-4758, Oak Ridge National Laboratory, January 1972.

26. Hobson, D.O., "Ductile-brittle behavior of Zircaloy fuel cladding," Proc. ANS Topical Mtg. on Water Reactor Safety, Salt Lake City, 26 March, 1973.
27. Pawel, R.E., "Oxygen diffusion in beta Zircaloy during steam oxidation," J. Nucl. Mater. 50 (1974) 247-258.
28. Sawatzky, A., "Proposed criterion for the oxygen embrittlement of Zircaloy-4 fuel cladding," Proc. 4th Symp. on Zirconium in the Nuclear Industry, Stratford-on-Avon, UK, 27-29 June, 1978.
29. Grandjean, C., "Oxidation and quenching experiments under simulated LOCA conditions with high burnup clad material," Proc. 24th Water Reactor Safety Information Meeting, Bethesda, USA, 21-23 October, 1996.
30. Grandjean, C. et al., "High burnup UO2 fuel LOCA calculations to evaluate the possible impact of fuel relocation after burst," ANL Program Review Meeting, Rockville (USA), 22 October, 1999.
31. Hofmann, P. et al., PECLOX: A Computer Model for the Calculation of the Internal and the External Zircaloy Cladding Oxidation, KFK-4422 Part 2, October 1988.
32. Uetsuka, H. et al., "Zircaloy-4 cladding embrittlement due to inner surface oxidation under simulated loss-of-coolant condition," J. Nucl. Sci. Tech. 18 (1981) 705-717.
33. Uetsuka, H. et al., "Embrittlement of Zircaloy-4 due to oxidation in environment of stagnant steam," J. Nucl. Sci. Tech. 19 (1982), 158-165.
34. Komatsu, K., "The effects of oxidation temperature and slow cooldown on ductile-brittle behavior of Zircaloy fuel cladding," Proc. CSNI Specialists' meeting on the behavior of water reactor fuel elements under accident conditions, Spaatind, Norway, 13-16 September, 1976.
35. Komatsu, K. et al., "Load-bearing capability in deformed and oxidized Zircaloy cladding," Proc. CSNI Specialist Mtg. on Safety Aspects of Fuel Behavior in Off-Normal and Accident Conditions, Espoo, Finland, 1-4 September, 1980.
36. Lorenz, R.A., "Fuel rod failure under loss-of-coolant conditions in TREAT," Nucl. Tech. 11 (1971) 502-520.
37. Haggag, F. M., Zircaloy-Cladding-Embrittlement Criteria: Comparison of In-Pile and Out-of-Pile Results, NUREG/CR-2757, July 1982.