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Stress Corrosion Cracking Failure Behavior of Zircaloy-4 Tubing at Elevated Temperatures

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Stress Corrosion Cracking Failure Behavior of Zircaloy-4 Tubing at Elevated Temperatures[1)]

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Summary

The paper summarizes the stress corrosion cracking (SCC) experiments performed with Zircaloy-4 at the Kernforschungszentrum Karlsruhe from 1975 to the present within the framework of the Nuclear Safety Project.

Of all the fission products produced in nuclear fuel, only iodine can influence the rupture stress, the circumferential burst strain, and the time-to-failure of Zircaloy-4 cladding. The mechanical properties of zircaloy are influenced only above a specific critical iodine concentration in the specimens, and only up to approximately 850°C. The critical iodine concentration which results in low-ductility failure of the cladding was therefore determined as a function of temperature (500 to 900°C) and compared with the estimated iodine concentration in LWR fuel rods. A comparison of these values shows that cladding failure due to iodine-induced SCC can be expected only below 700°C. Above 700°C, the threshold iodine concentration is higher than the estimated amount of iodine available. This is in agreement with the results of in-pile LOCA tests performed in the FR 2 reactor with high burnup fuel rods (35000 MWd/t_U). The iodine-induced low-ductility failure behavior of zircaloy tubing can be described by fracture mechanics methods, using a modified version of the stress-intensity factor K_I-concept of LEFM to predict times-to-failure.

In addition, basic experiments to investigate the iodine/zirconium chemical interaction and the decomposition behavior of CsI by various oxygen potentials have been performed. The results show that elemental iodine reacts completely with zirconium to form gaseous zirconium tetraiodid (ZrI_4) and various condensed ZrI_x-phases whose chemical compositions depend on temperature and initial iodine concentration. The gaseous ZrI_4 is probably responsible for stress corrosion crack initiation and propagation. The estimated critical ZrI_4 pressures above which low-ductility SCC failure of zircaloy tubing always occurs varies between 5 mbar at 550°C and 43 mbar at 800°C. Extrapolation of these values to lower temperatures and comparison with literature data show good agreement. CsI can decompose at rather low oxygen potentials resulting in a sufficient iodine activity to cause low-ductility SCC failure of the cladding.

Spannungsrißkorrosionsverhalten von Zircaloy-4-Hüllrohren bei erhöhten Temperaturen

Zusammenfassung

Dieser Bericht faßt die Ergebnisse von Spannungsrißkorrosions (SRK)-Experimenten mit Zircaloy-4-Hüllrohren zusammen, die seit 1975 im Kernforschungszentrum Karlsruhe im Rahmen des Projektes Nukleare Sicherheit durchgeführt wurden.

Von allen im Brennstoff entstehenden Spaltprodukten besitzt nur Jod einen Einfluß auf die Bruchfestigkeit, die Berstdehnung und die Standzeit von Zircaloy-4 (Zry)-Hüllrohren. Die mechanischen Eigenschaften von Zry werden jedoch nur oberhalb einer spezifischen kritischen Jodkonzentration in den Versuchsproben bis maximal etwa 850^{o}C beeinflußt. die kritische Jodkonzentration, die zum verformungsarmen Versagen des Hüllrohres führt, wurde deshalb in Abhängigkeit der Temperatur (500-900^{o}C) bestimmt und mit der Jodkonzentration in LWR-Brennstäben verglichen. Der Vergleich zeigt, daß ein Hüllrohrversagen infolge jodinduzierter SRK nur unterhalb 700^{o}C erwartet werden kann. Oberhalb 700^{o}C ist die notwendige kritische Jodkonzentration größer als die im Brennstab zu erwartende. Dies ist in Übereinstimmung mit den Versuchsergebnissen von in-pile LOCA-Experimenten, die im FR 2 mit hochabgebrannten Brennstäben (35000 MWd/t_U) durchgeführt wurden. Das SRK-Verhalten von Zry-Hüllrohren kann mit Hilfe bruchmechanischer Methoden beschrieben werden. Eine modifizierte Version des Spannungsintensitätsfaktor-K_I-Konzepts der LEFM ist geeignet, die Standzeit vorherzusagen.

Außerdem erfolgten Experimente zum Studium der chemischen Jod/Zry-Wechselwirkungen und des Aufspaltungsverhaltens von CsJ durch unterschiedliche Sauerstoffpotentiale. Elementares Jod reagiert vollständig mit dem Zirkonium unter Bildung von Zirkoniumtetrajodid (ZrJ_4) und verschiedenen kondensierten ZrJ_x-Phasen. Das gasförmige ZrJ_4 ist sehr wahrscheinlich für die Rißbildung und Rißausbreitung verantwortlich. Die kritischen ZrJ_4-Drücke, oberhalb derer ein verformungsarmes Versagen der Zry-Hüllrohre infolge SRK erfolgt, variieren zwischen 5 mbar bei 550^{o}C und 43 mbar bei 800^{o}C. Die Extrapolation dieser Daten zu niedrigen Temperaturen und ein Vergleich mit Literaturdaten zeigen eine gute Übereinstimmung. CsJ kann sich bereits bei relativ niedrigen Sauerstoffpotentialen zersetzen und die resultierende Jodaktivität kann ein verformungsarmes Versagen des Hüllrohres infolge SRK bewirken.

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1. Introduction

The fuel elements of a nuclear power reactor undergo various chemical and mechanical loads during normal operation, and especially during transient conditions. In the course of nuclear fission of UO_2 or $(U,Pu)O_2$, about 30 different fission product elements are formed, and oxygen is released. Some of the fission products are volatile and can therefore escape from the fuel and may react with the cladding during irradiation. With increasing burnup, the gap between the fuel and cladding narrows as a result of cladding creepdown, fuel swelling, and relocation, and ultimately disappears. Then, in addition to chemical interactions, there will be pellet-cladding mechanical interactions (PCI). Mechanical interactions are most evident when the reactor power is increased because the fuel thermally expands more than the cladding. Moreover, in transients under accident conditions the cladding temperature increases which results in stronger chemical interactions and in a decrease of cladding strength. For reasons of safety, it is therefore of great importance to know how Zircaloy-4 cladding behaves with respect to the combined chemical and mechanical loads at elevated temperatures under ATWS (Anticipated Transient without Scram) and LOCA (Loss-of-Coolant Accident) conditions.

The purpose of this paper is to present a survey of the Zircaloy-4 stress corrosion cracking (SCC) experiments performed between 500 and 900°C at the Kernforschungszentrum Karlsruhe within the framework of the Project "Nukleare Sicherheit" (PNS) from 1975 to the present. The paper describes out-of-pile experiments performed with as-received and preflawed Zircaloy-4 tube specimens to: (a) determine which fission products, besides iodine, can influence cladding burst strain and time-to-failure, (b) determine the critical iodine concentration resulting in low-ductility stress corrosion cracking failure, (c) determine the zirconium/iodine reaction products as a function of temperature, (d) describe the iodine-induced SCC growth by fracture mechanics methods, and (e) show the relevance of the results with respect to transient fuel rod behavior. The detailed results are (or will be) published in References /1/ through /8/.

2. Experimental Procedure

Creep rupture tests as well as temperature and pressure transient burst tests were performed with unirradiated Zircaloy-4 tube specimens (10.76 x 0.72 mm; 60 to 600 mm long). The specimens were filled with simulated fission product elements or compounds, closed and welded in gloveboxes under very pure inert gas conditions. The simulated fission product concentration varied between 0.3 and 610 mg/cm^3 (1 cm^3 corresponds roughly to 1.47 cm tube length or 4.29 cm^2 of inner cladding surface). The experiments were performed primarily under inert gas conditions /1, 3-8/ with some of the experiments performed in steam /2/. The test specimens were heated in inert gas using thermal radiation, and in steam using a central heater (fuel rod simulator). The cladding tubes were subjected to mechanical loading using internal helium pressure. The burst temperatures varied between 500 and 900^{o}C. Internal pressure and cladding temperature were measured continuously throughout the test. In addition creep rupture experiments were performed under controlled ZrI_4 partial pressure conditions /5/.

After the tests, the specimens were investigated metallographically and by scanning electron microscopy (SEM). Some of the reaction products formed were analyzed chemically by X-ray diffraction studies and by X-ray fluorescence analysis.

The extent of Zircaloy-4 "embrittlement" was determined by comparing the results of specimens containing fission products with reference specimens containing He in terms of burst strain, time-to-failure, and morphology of the fracture surface. The term embrittlement is used simply to denote a reduction in ductility, and is not intended to imply that the fracture process necessarily occurs in a completely brittle mode.

3. Experimental Results

3.1 Creep Rupture Experiments in the Presence of Simulated Fission Products

The results of creep rupture tests with preflawed Zircaloy-4 tube specimens containing small amounts of simulated fission product elements or compounds are presented in figure 1 /2/. The changes in circumferential

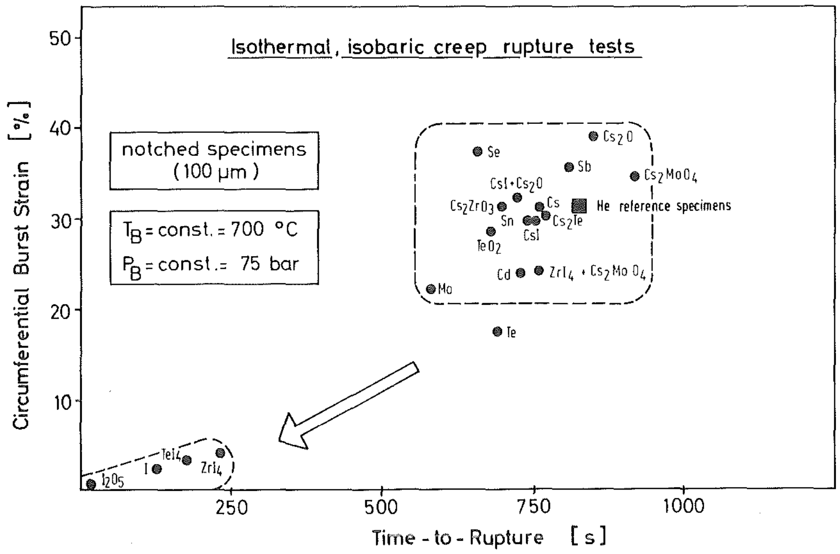


Figure 1: Effect of simulated fission products on the circumferential burst strain and time-to-failure of Zircaloy-4 tubing at 700°C in He (preflawed specimens).

burst strain and time-to-failure due to the fission products were determined by comparison with helium-filled reference specimens containing no fission products. The simulated fission products all caused some change with respect to time-to-failure and burst strain. However, only the specimens containing elemental iodine or volatile iodine compounds (I_2O_5, ZrI_4, TeI_4) exhibited a marked reduction in burst strain for both types of specimens (as-received, preflawed). The preflawed specimens also showed a strong decrease in time-to-failure (fig.1) /2/.

In contrast to the other iodides examined, CsI alone did not exert any influence on the mechanical properties of zircaloy. However, laboratory experiments with CsI conducted at different oxygen potentials have shown that decomposition of CsI can take place at a sufficiently fast rate that, even in transient burst experiments (time-to-failure < 80 s), zircaloy tubing fails as a result of iodine-induced SCC /7/. Various metal/metal oxide mixtures and hyperstoichiometric UO_{2+x} with different O/U-ratios were used to set the oxygen potentials in these experiments. In some cases, other simulated fission products were also present to allow the formation of complex compounds such as cesium molybdate (Cs_2MoO_4). In the (UO_{2+x} + CsI + Mo) or ($UO_{2.00}$ + CsI + Mo/MoO_2) systems, Cs_2MoO_4 can form at rather low oxygen potentials (≈ -400 kJ/mol O_2), thus decomposing the CsI. The resultant iodine partial pressure was sufficiently high to cause low-ductility failure of zircaloy tubing due to iodine-induced SCC (fig.2) /7/. Equilibrium calculations of the iodine partial pressure (iodine activity) in the fuel/fission product system UO_2/CsI/Mo confirms these experimental results /9/.

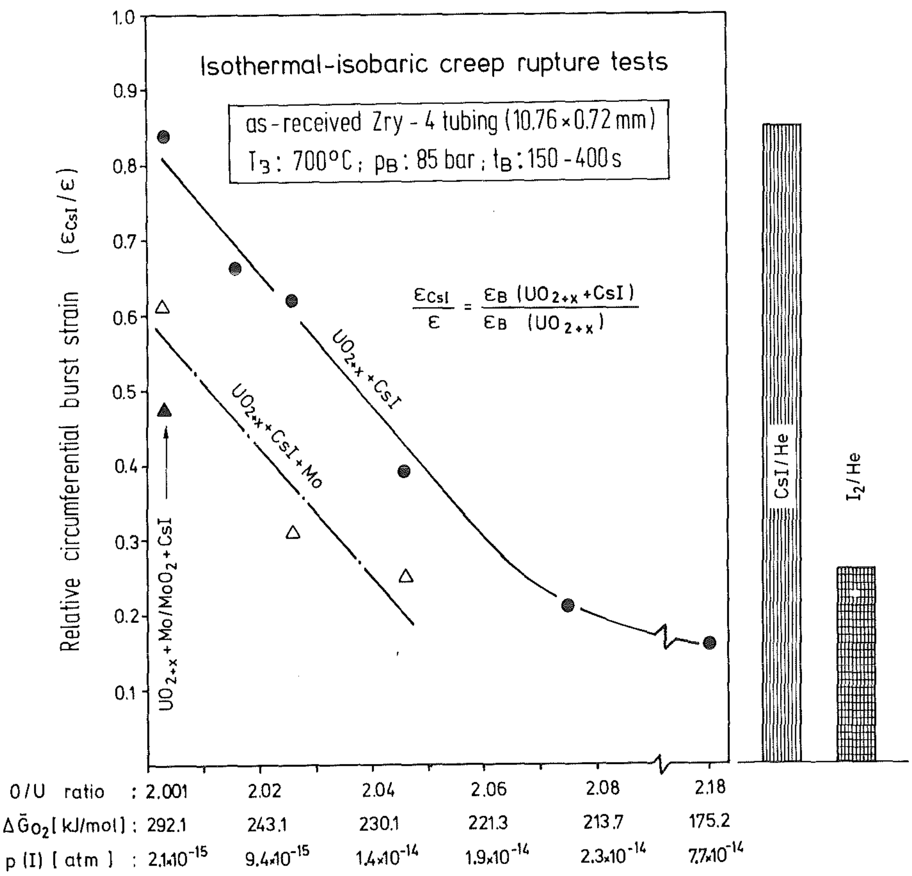


Figure 2: Stress corrosion cracking failure of Zircaloy-4 tubing due to iodine released from CsI in the presence of UO_{2+x}, UO_{2+x} + Mo, and UO_{2+x} + Mo/MoO_2 at 700°C.

The tangential fracture or hoop stress at rupture was calculated for each of the transient burst and isothermal creep rupture specimens from the burst strain and is graphed in figure 3. The tangential fracture

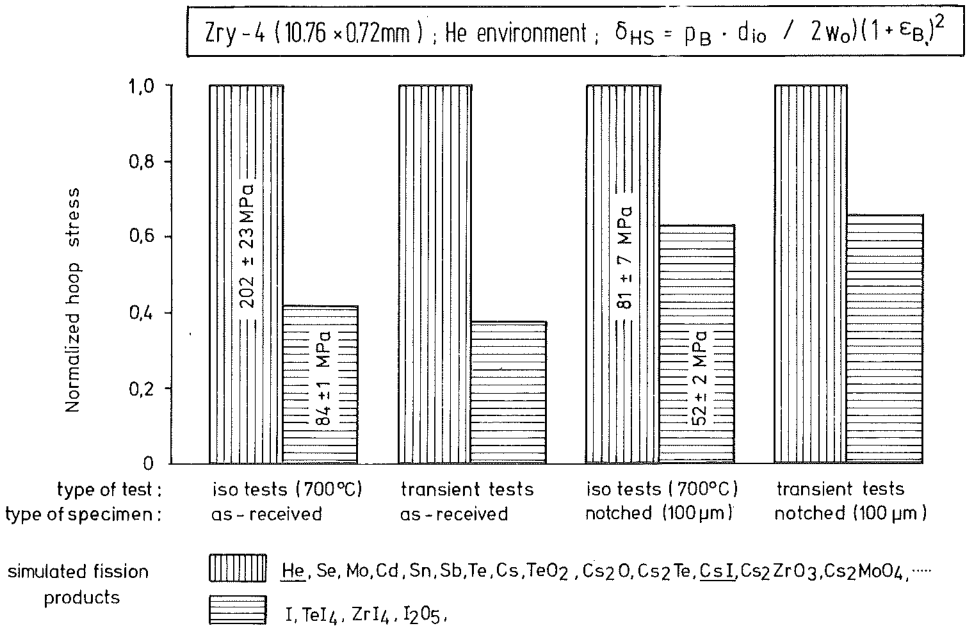


Figure 3: Influence of simulated fission products on the hoop stress of Zircaloy-4 tubing. Only the volatile iodine compounds cause a reduction in burst strength.

stress was much smaller for the specimens containing I_2, TeI_4, ZrI_4 or I_2O_5 than for the helium reference specimens or the specimens containing other simulated fission products. The fracture stress can be considered as the critical threshold stress which, in the presence of iodine, results in low-ductility SCC failure of Zircaloy-4 cladding. The critical stress levels determined for these tests are well below the normal fracture stress levels of Zircaloy-4 tubing /1,2/.

SEM examinations revealed that, due to the action of iodine in cooperation with stress, a great number of incipient cracks of different sizes had formed on the cladding inside surface (fig.4).

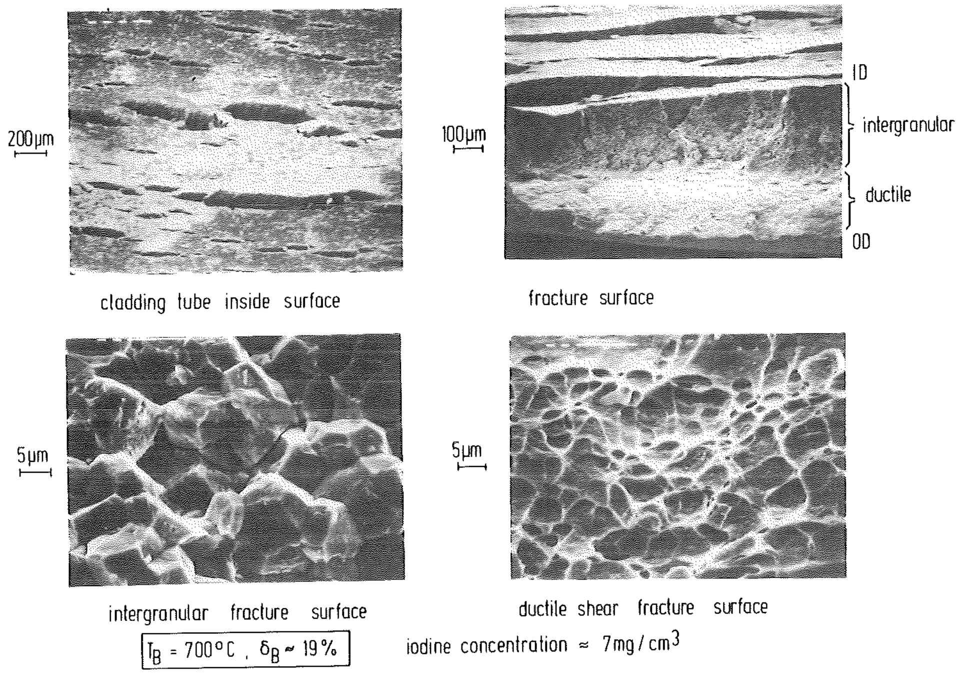


Figure 4: Zircaloy-4 cladding tube inside surface and fracture surface after failure under argon-iodine gas pressurization (as-received specimen).

These incipient cracks were observed over the entire circumference and length of the specimens. All of the cracks were axially oriented. As the cracks grow axially, they simultaneously penetrate radially into the cladding so that the stress immediately ahead of the crack tip and in the remaining tube cross section rises continuously. As soon as a critical crack depth is attained, the ultimate tensile strength of the Zircaloy is reached and instantaneous fracture of the remaining wall occurs. At 700^{o}C the crack formation caused by iodine is primarily intergranular, and the fracture of the remaining cladding wall is ductile (fig.4) /1,2,3/.

The fracture mode observed within the SCC zones was found to depend exclusively on temperature, and to be independent of iodine concentration. Above 600^{o}C, where zircaloy recrystallization took place during heating and a new structure of polyhedral grains was formed, the fracture occured by intergranular cracking. Below 600^{o}C, where the original texture was not modified during heating and the grains remained elongated in the axial direction, the fractures occured by transgranular cleavage and fluting. A mixture of both types of fracture was found at 600^{o}C, which therefore appeared to mark the transition temperature between transgranular and intergranular cracking under these conditions. The typical types of SCC fracture surfaces obtained between 500 and 700°C are shown in figure 5 /3/.

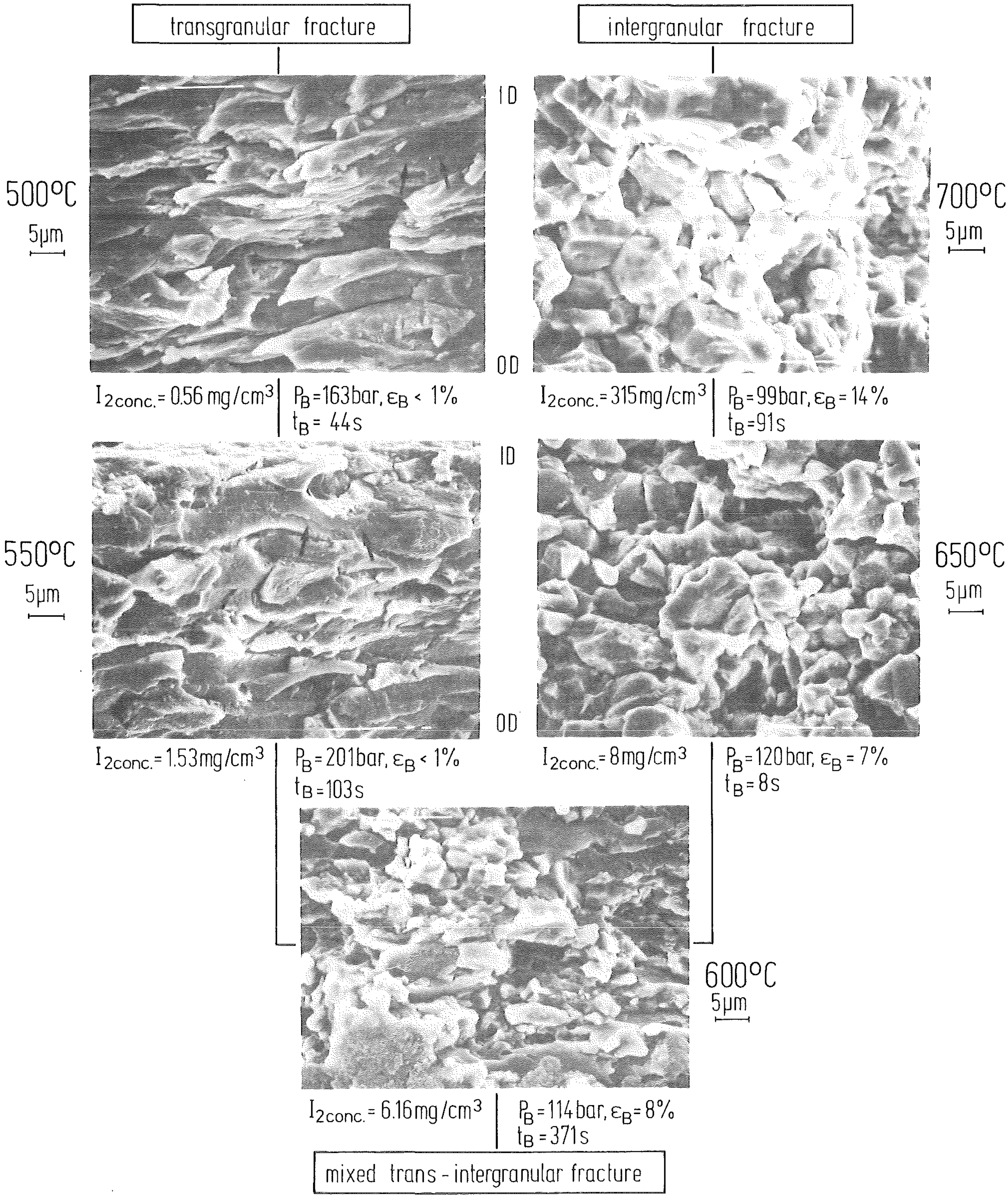


Figure 5: Brittle fracture types of as-received Zircaloy-4 tubes in an iodine environment as a function of temperature.

3.2 Determination of the Critical Iodine Concentration

Although only iodine has a pronounced influence on the burst strain, the burst strain is significantly reduced only after a specific iodine concentration within the tube specimens has been exceeded. Therefore, the critical iodine concentration which results in low-ductility SCC failure of Zircaloy-4 was determined as a function of temperature, and these values were compared with those expected in a fuel rod during reactor transient and accident conditions. The experiments were performed between 500 and 900^{o}C. The initial iodine concentrations varied between 0.01 and 300 mg/cm^3 (0.0023 to 6.9 mg/cm^2) [1 mg iodine per cm^3 correspond to a simulated burnup of 1.6 at % assuming total release of iodine from UO_2].

In figure 6,relative circumferential burst strain is plotted versus iodine concentration for the entire temperature range examined. All of the curves show a bimodal behavior which indicates that, for each temperature, whithin which the reduction in burst strain of zircaloy tubing takes place. Outside the critical region, burst strain appears to depend only slightly on iodine concentration /3/. The iodine-induced ductile-to-brittle transition in zircaloy is very pronounced between 500 and 800^{o}C. At higher temperatures, the transition is less pronounced and the reduction in burst strain is much smaller. This is one of the indications that iodine-induced SCC failure of zircaloy tends to disappear at higher temperatures. In figure 7 the relative, hoop stress is plotted as a function of temperature. The reduction in ductility due to iodine is especially strong between 700 and 800^{o}C /3/.

Three different pressures were examined at 700^{o}C and 800^{o}C to determine the influence of initial stress level on overall rupture behavior as a function of initial iodine concentration. The higher pressure caused a more abrupt change in ductility within the critical iodine region, i.e., a larger reduction in burst strain in a more narrow interval, but the mean position of the critical iodine concentration was unaltered (fig.8) /3/.

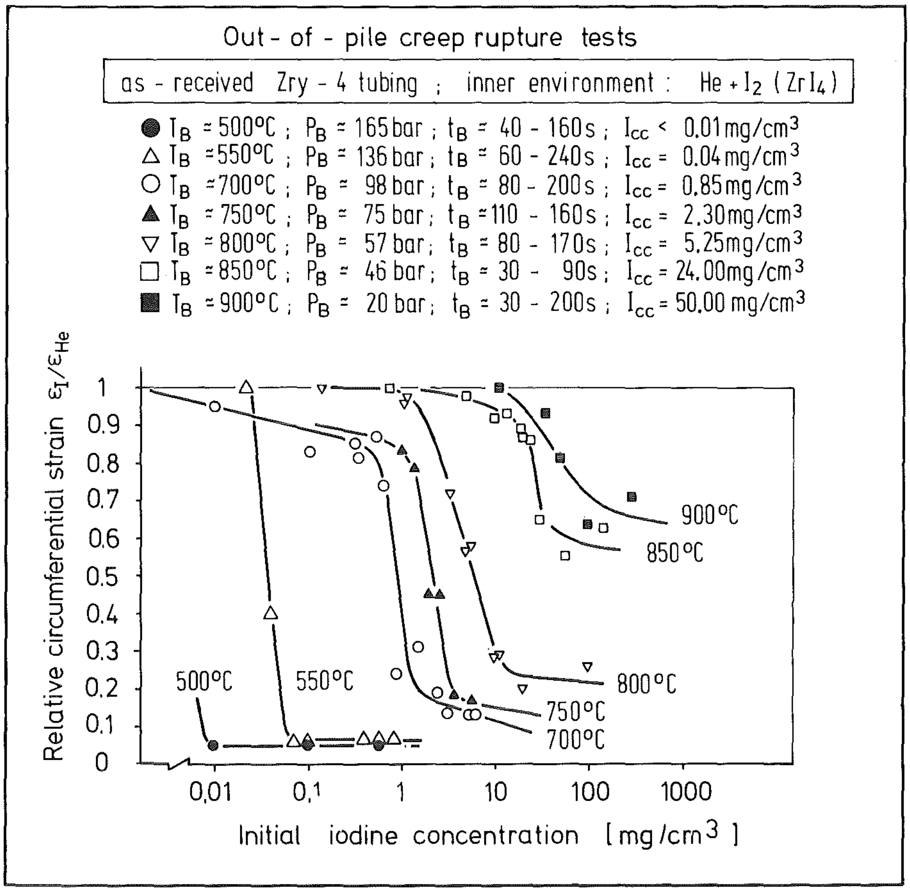


Figure 6: Influence of initial iodine concentration on burst strain of as-received Zircaloy-4 tubing between 500 and 900^{0}C.

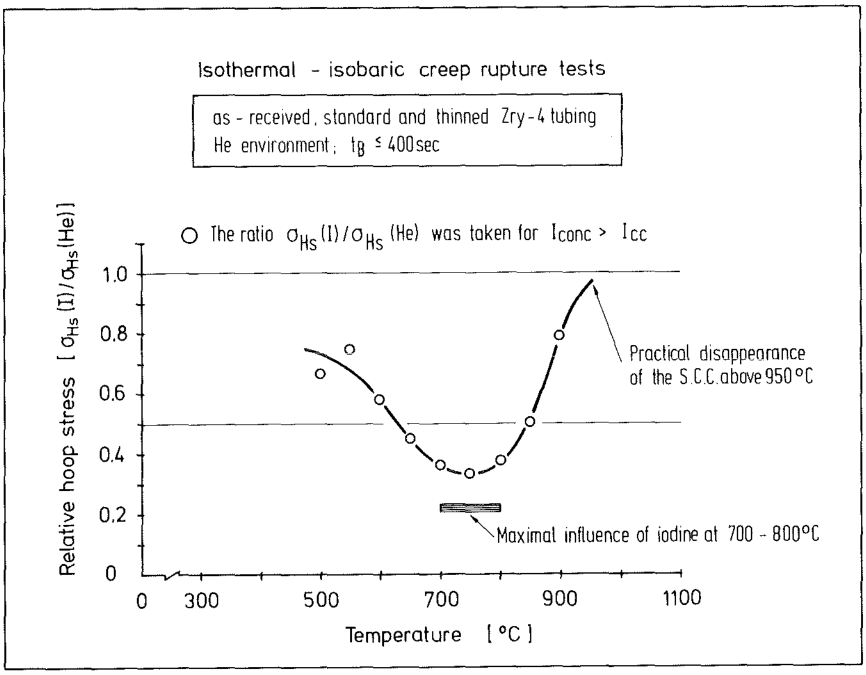


Figure 7: Influence of iodine on the rupture stress of as-received Zircaloy-4 tubing between 500 and 900^{0}C.

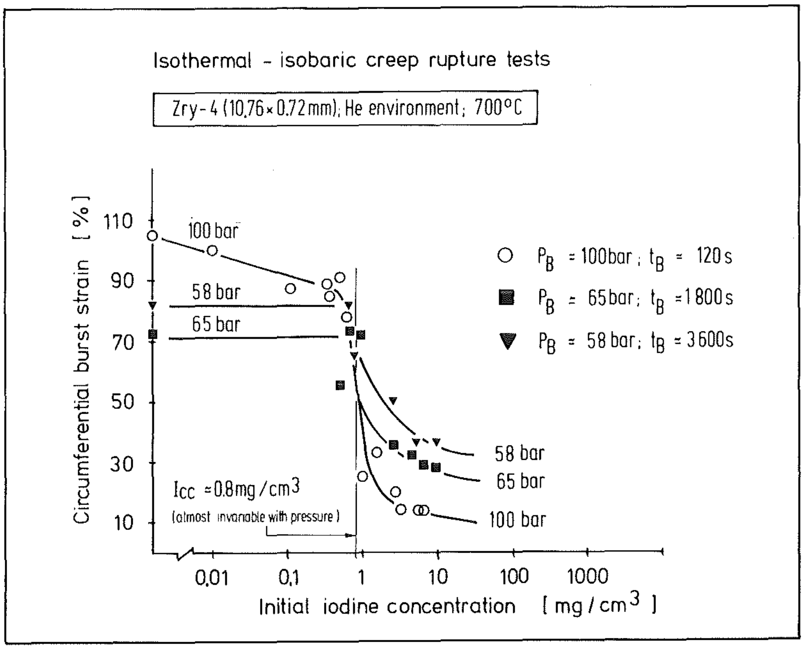


Figure 8: Effect of burst pressure on burst strain and critical iodine concentration of Zircaloy-4 tubing at 700°C.

At all temperatures examined, iodine caused the formation of incipient stress corrosion cracks even at the lowest concentrations where no influence on overall burst deformation was evident. Metallographic and SEM examinations revealed numerous iodine-induced cracks on the cladding inside surface. These small incipient cracks grew in depth with increasing iodine concentration /3/. Figure 9 shows cross sections of two ruptured tube specimens and the rupture sizes in greater detail. The He-reference specimens (and specimens containing iodine below the critical concentration in which cracks cannot propagate due to iodine starvation) show normal plastic deformation followed by local necking and ductile fracture. In tube specimens containing iodine low-ductility SCC failure occured, i.e., the tubing failed after only slight deformation with almost no local necking. The iodine-induced fracture occurs normal to the direction of the tangential stress /1,2,3/.

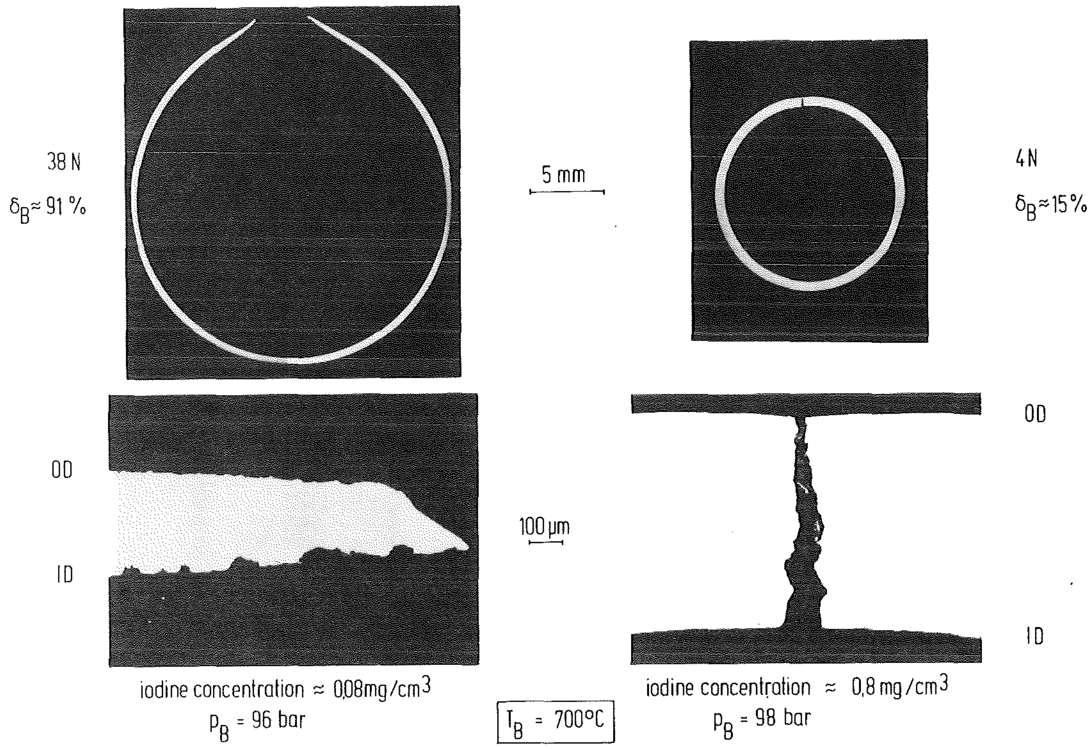


Figure 9: Cross sections of failed as-received Zircaloy-4 tubing. Influence of the iodine concentration on type of fracture at 700^oC. $I_c < I_{cc}$: ductile failure; $I_c > I_{cc}$: low-ductility failure.

To analyse the temperature dependence, the critical iodine concentration was defined as the value at which the differential burst strain was reduced by about 50%. The critical iodine concentration values increase very rapidly with temperature, with an overall variation of about 4 orders of magnitude over the entire temperature range (< 0.01 mg/cm^3 at 500^oC to 50 mg/cm^3 at 900^oC). The very low values obtained up to 550^oC ($\lesssim 0.04$ mg/cm^3) demonstrate the high sensitivity of zircaloy to iodine-induced SCC at temperatures slightly above normal reactor operating temperatures. A plot of the critical iodine concentration versus reciprocal temperature is shown in figure 10, with low-temperature data from the literature (as summarized in /3/) for comparison. The curve has different slopes in different temperature regions indicating that, in principle, different reactions take place in the different regions. In the low-temperature region (300 to 400^oC), a great variation in the data from the literature exists.

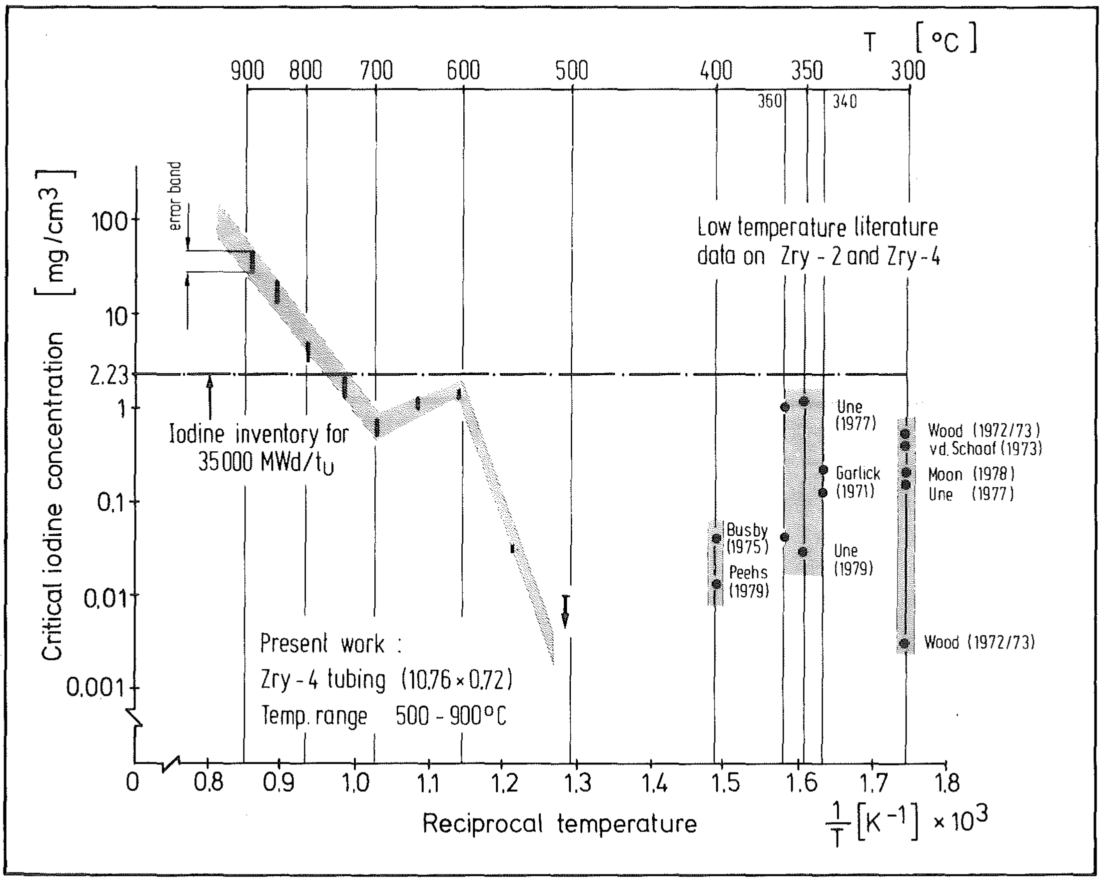


Figure 10: Plot of the critical iodine concentration, resulting in SCC failure of as-received Zircaloy-4 tubing, versus reciprocal temperature between 500 and 900^{0}C.

The iodine reacted at all temperatures with the zirconium to form gaseous ZrI_4 and solid zirconium iodides (ZrI_x). It is believed that stress corrosion crack initiation and propagation are caused primarily by gas adsorption processes. It is therefore appropriate to relate SCC failure to ZrI_4 pressure. However, if all of the initial iodine concentration would be converted to a corresponding ZrI_4 pressure and no condensed phases are considered, a plot similar to figure 10 is obtained (see fig.12) /3/. It was therefore important to estimate the actual ZrI_4 pressures inside the tube specimens as a function of temperature.

3.3 Estimation of ZrI_4 Pressures Causing Low-Ductility Failure

Zircaloy/iodine reaction experiments were performed to determine the actual amount of gaseous ZrI_4 and the amount and chemical composition of the corresponding condensed ZrI_x phases as functions of iodine concentration and temperature /5/. The results are shown in figure 11.

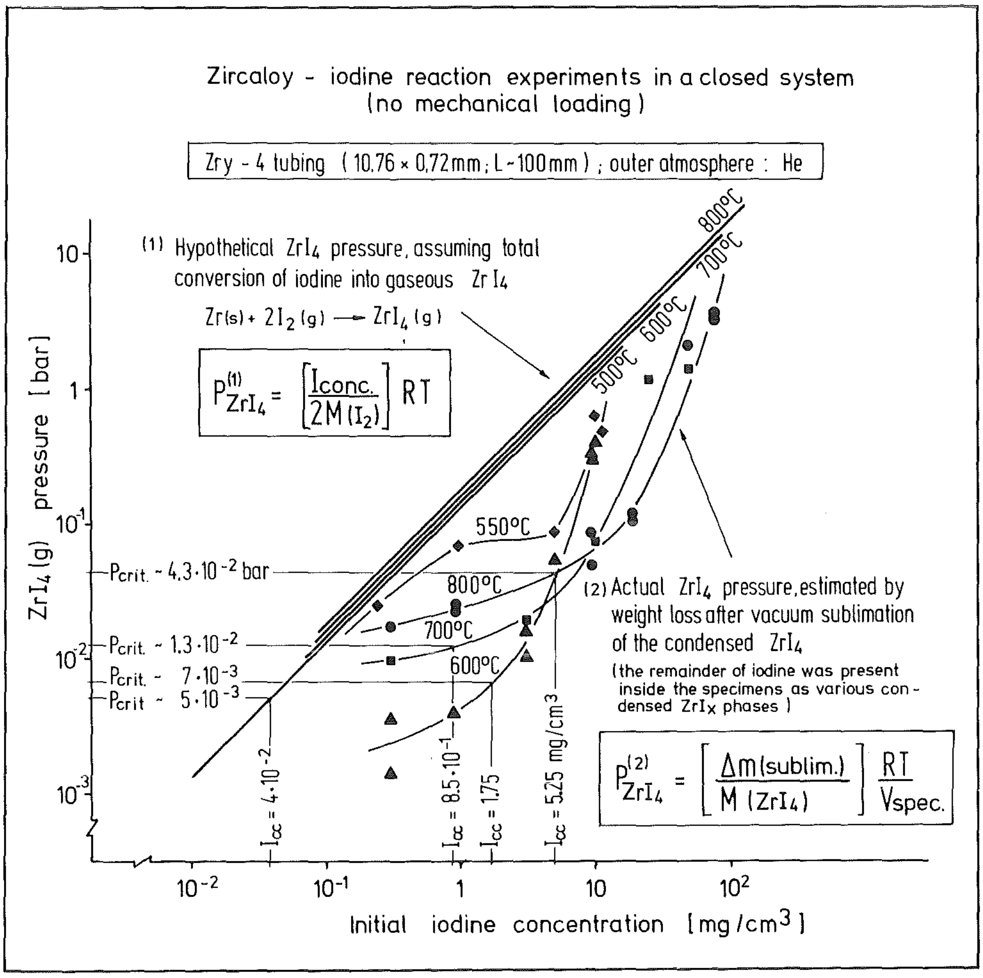


Figure 11: ZrI_4 gas pressure as function of initial iodine concentration and temperature (comparison between hypothetical and actual ZrI_4 pressure).

The ZrI_4 gas pressure was calculated from the sublimated ZrI_4 mass (the ZrI_4 gas phase was sucked off the specimens, condensed, and weighed). The amount (weight) and crystallographic data of the condensed ZrI_x phases are given in /5/. The values calculated from the sublimated amoutns of ZrI_4 are referred to in the figure 11 as the "actual" ZrI_4

pressures. The figure also shows the "hypothetical" ZrI_4 pressures (straight lines) which were calculated assuming that all of the initial amount of iodine reacted with Zr to form gaseous ZrI_4, and no condensed ZrI_x phases formed. The results show that, at all temperatures, a strong reduction of the initally high ZrI_4 pressure occurred due to the formation of solid ZrI_x (probably nonequilibrium) phases. The reduction is especially pronounced in the range of iodine concentrations which result in low-ductility SCC failure of zircaloy tubing (0.041 $\leq$ critical iodine concentration $\leq$ 5.25 mg/cm^3). The corresponding critical ZrI_4 pressures are 5 mbar at 550°C, 7 mbar at 600°C, 13 mbar at 700°C, and 43 mbar at 800°C (fig.11).

The volatility of the condensed ZrI_x phases was expected to be very low, and it was doubtful whether these phases could deliver sufficient gaseous iodine-containing species (for example ZrI_4) to the tip of propagating cracks since the times-to-failure were relatively short ($\leq$ 500 s). Several specimens were therefore pressurized with He after the gaseous ZrI_4 phase was removed. The failure behavior at all test temperatures was very similar to specimens tested with very little or no iodine. There was practically no influence of the condensed, solid ZrI_x phases on burst strain and time-to-failure. Only very smal incipient cracks formed on the cladding inside surface, and did not propagate because the condensed ZrI_x phases could not deliver sufficient amounts of gaseous ZrI_4 to the crack tips. The fracture surfaces exhibited typical ductile failure characteristics (dimples) /5/.

The estimated (actual) and calculated (theoretical) ZrI_4 values are plotted in figure 12 as functions of reciprocal temperature for the range 500 to 900°C (the present work) and for lower temperatures examined by other authors (300 to 400°C). The estimated critical ZrI_4 pressures (thick dashed line) are lower than the calculated ZrI_4 pressures (thick solid line) due to the partial consumption of iodine by the formation of solid ZrI_x phases (fig.12). The actual critical ZrI_4 pressures show uniform temperature dependence over the whole range of temperatures. The discontinuity in the theoretical critical ZrI_4 pressures between 600 and 700°C (as in figure 10) corresponds to the greater

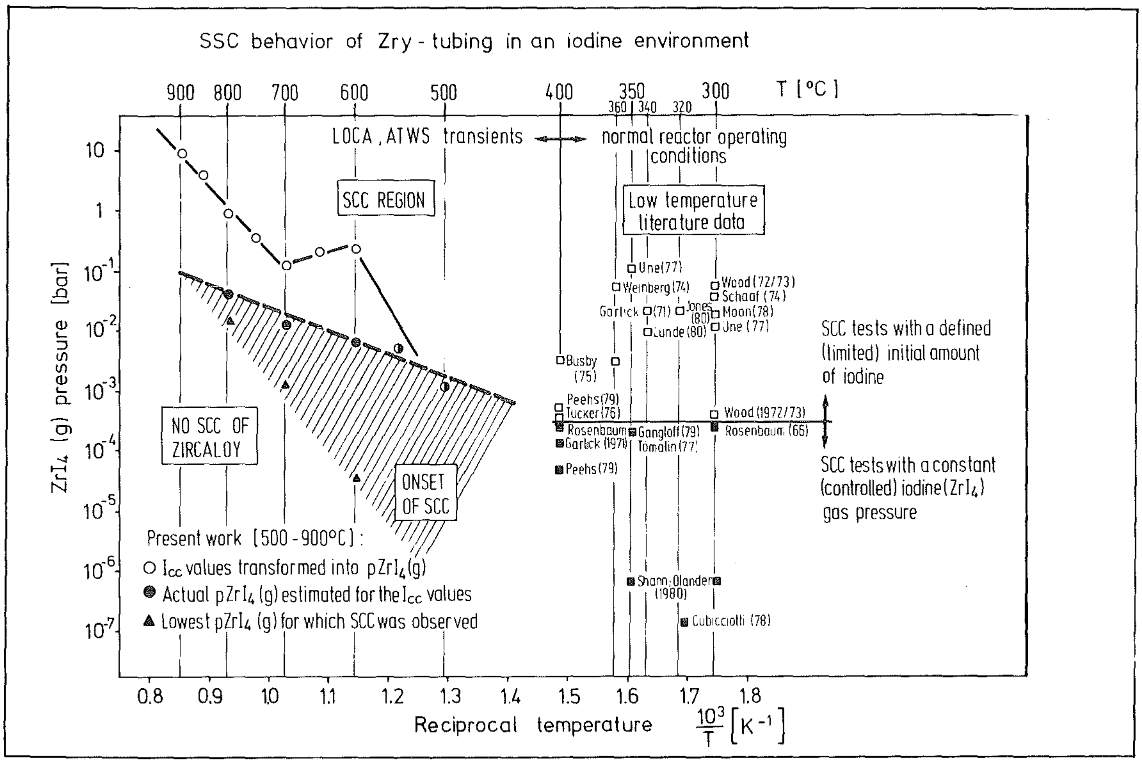
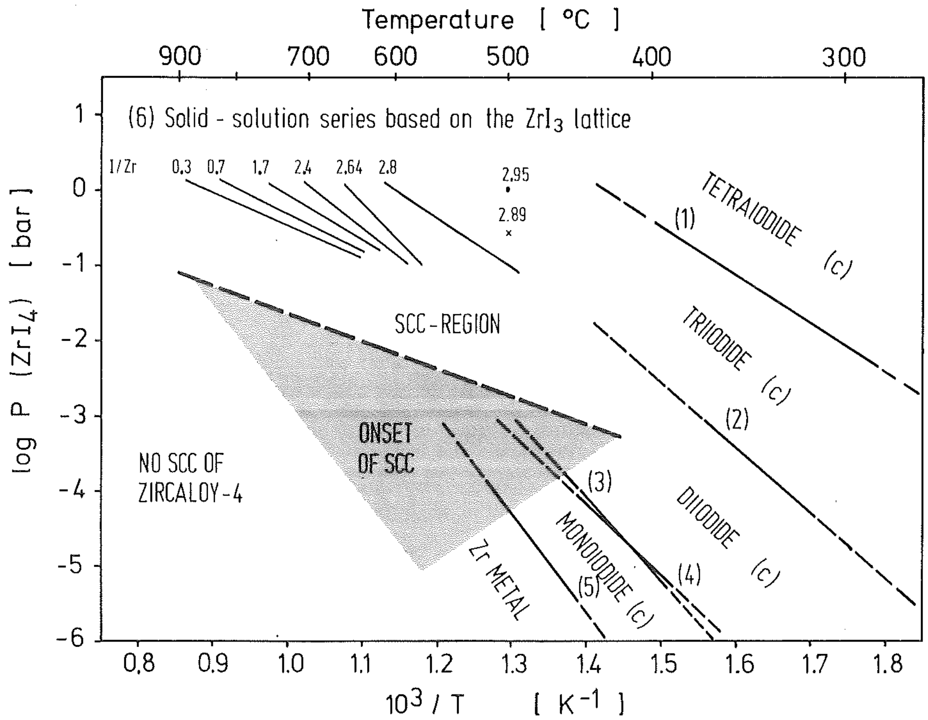


Figure 12: ZrI_4 gas pressures resulting in SCC failure of zircaloy tubing from 300 to 900°C.

consumption of iodine by the formation of the corresponding condensed phases at 600°C (fig.11) /5/. It must be emphasized that the critical ZrI_4 pressures determined in SCC tests conducted with limited amounts of iodine are conservative maximum values above which low-ductility SCC failure of zircaloy will always occur, and that below these values a rather wide range of ZrI_4 pressures exists where onset of SCC can be observed (fig.12). Extrapolation of the actual critical ZrI_4 pressures from high temperatures shows reasonable agreement with other test results from the literature for SCC tests performed with constant ZrI_4 gas pressures. There exist a great scatter in the literature data of about 6 orders of magnitude with respect to the critical ZrI_4 pressures (fig.12).

Assuming equilibrium conditions for the chemical interaction between an iodine-containing gas species and zirconium, the relationships between gaseous ZrI_4 and the condensed, solid ZrI_x phases are given in figure 13. According to figure 13 gaseous ZrI_4 should be in equilibrium



Equilibrium lines :

(1) ZrI_4 (c) / ZrI_4 (g) [558 - 671 K] - O.Rahlfs, W.Fischer (1933)
(2) ZrI_3 (c) / $ZrI_{3.2}$ (c) [586 - 641 K] - M.A.Bhatti et al (1977)
(3) $ZrI_{1.6}$ (c) / $ZrI_{2.8}$ (c) [663 - 723 K] - ibid
(4) $ZrI_{1.3}$ (c) / $ZrI_{1.9}$ (c) [660 - 720 K] - D.Cubicciotti, H.Lau (1979)
(5) $ZrI_{1.05}$(c) / ZrI (c) [720 - 790 K] - D.Cubicciotti, H.Lau (1981)
(6)* ZrI_3 (c) / $ZrI_{0.3}$ (c) [773 -1123 K] - Kh.S.Lopis et al (1979)
*(single phase region, no monovariant behavior)

Figure 13: ZrI_4 gas pressure in equilibrium with various solid ZrI_x phases versus the reciprocal temperature. Indication of a ZrI_4 pressure region which results in SCC failure of Zircaloy-4 tubing.

with chemisorbed iodine below the equilibrium ZrI_4 pressure over the univariant Zr/ZrI phase region, and not with zirconium (sub) iodides. However, condensed zirconium iodides were always found in these experiments even above 600°C (temperature at which the critical ZrI_4 pressure line crosses the Zr/ZrI equilibrium line) where no condensed iodides should exist. Possibly, zirconium subiodides form only above a certain temperature where the reaction kinetics are favorable.

In an actual fuel rod containing UO_2, the chemical interaction of iodine with zircaloy cladding, which results in the formation of gaseous ZrI_4 and various condensed ZrI_x phases or chemisorbed layers of iodine, probably does not occur in the same way. In the presence of UO_2, an oxygen potential exists which can prevent the formation of ZrI_x compounds, depending on the temperature, because ZrO_2 is thermodynamically more stable than the zirconium iodides. Therefore, SCC failure in the presence of UO_2 is probably caused by gaseous elemental iodine, at least at higher temperatures (> 600°C). At lower temperatures, the extent of the chemical interaction between iodine and/or oxygen and zirconium depends on the reaction kinetics. At low temperatures ($\lesssim$ 400°C), the iodine/Zr reactions are apparently favored over the oxygen/Zr reaction, i.e., gaseous ZrI_4 rather than elemental iodine is probably responsible for SCC failure /6/.

3.4 Fracture Mechanics Analysis of Iodine-Induced Crack Growth

Since the Zircaloy-4 tubing fails in a "brittle" mode due to iodine-induced SCC, the time-to-failure can be predicted by fracture mechanics methods. The model was verified by isothermal, isobaric creep rupture tests with preflawed tube specimens. The initial notch depth varied between 50 and 200 μm, with a notch length equal to 100 times the notch depth. The experiments were performed in the temperature range 500 to 700°C. The time-to-failure varied between 5 and 3600 s /8/.

The failure behavior is determined primarily by two processes:
(a) plastic creep strain in the whole cladding wall which takes place predominantly during the crack formation phase (incubation period); and (b) crack propagation which is influenced by the temperature-dependent transport velocity of gaseous iodine and the tendency of iodine to be adsorbed at the crack tip. The temperature-dependent combination of the two processes and additional local plastic strains in the vicinity of the crack front, particularly at 600°C, determine the strain and time-to-failure behavior of the tubular specimens.

The time-to-failure behavior of iodine-containing Zircaloy-4 cladding tubes from 500 to 700^{0}C can be described by an elastic-plastic fracture mechanics model. The model includes an empirically-determined computation method for the incubation period, as a portion of the time-to-failure, as well as an elastic-plastic model for describing crack growth due to iodine-induced SCC. The total service life of the cladding tube is obtained by adding the incubation period for crack formation to the time of crack growth. The incubation period is a temperature-dependent function of both the depth of surface damage (both fabrication pits and machined notches) and the load, and is 40 to 90% of the time-to-failure. The elastic-plastic crack growth model is a modified version of the stress intensity K_I-concept of linear-elastic fracture mechanics. The extensions of this concept take into account a plastic strain zone ahead of the crack tip, which effectively increases the crack depth, and, in addition, a dynamic correction factor to the crack geometry which is essentially a function of the effective crack depth. Unstable crack growth is predicted to occur when the residual cross section reaches plastic instability.

Model results show good agreement with experimental data at 500, 600, and 700^{0}C. The crack velocity at all three temperatures is a clear power function of stress intensity ahead of the crack tip; the exponent is 4.9. The growth rate for iodine-induced SCC ban be described by an Arrhenius-type rate equation

$$\left(\frac{da}{dt}\right)_{500-600^{0}C} = 1.17\cdot 10^{7} \exp\left(\frac{-2.39\cdot 10^{5}}{R\cdot T}\right) K_I^{4.9}$$

where da/dt is in [m/s], $K_{I,eff}$ in [MPa$\cdot$m$^{1/2}$], and R is 8.3143 [J/mol$\cdot$K]. The model can estimate time-to-failure of iodine-containing as-received cladding tubes within a factor of 2. Application of the model to temperatures below 500^{0}C is possible in principle. Due to the increasing scatter in experimental data, the structural transformation of the cladding by recrystallization, and the growing importance of creep strain, the model has an upper temperature limit of approximately 650^{0}C. The model is suitable for use in computer codes describing LWR fuel rod behavior in transients and accidents.

Model results at 500, 600, and 700°C are shown with similar literature data at lower temperatures in figure 14. For a given stress intensity factor, the crack growth rate increases with increasing temperature. The crack growth rates from 500 to 700°C agree well with those from

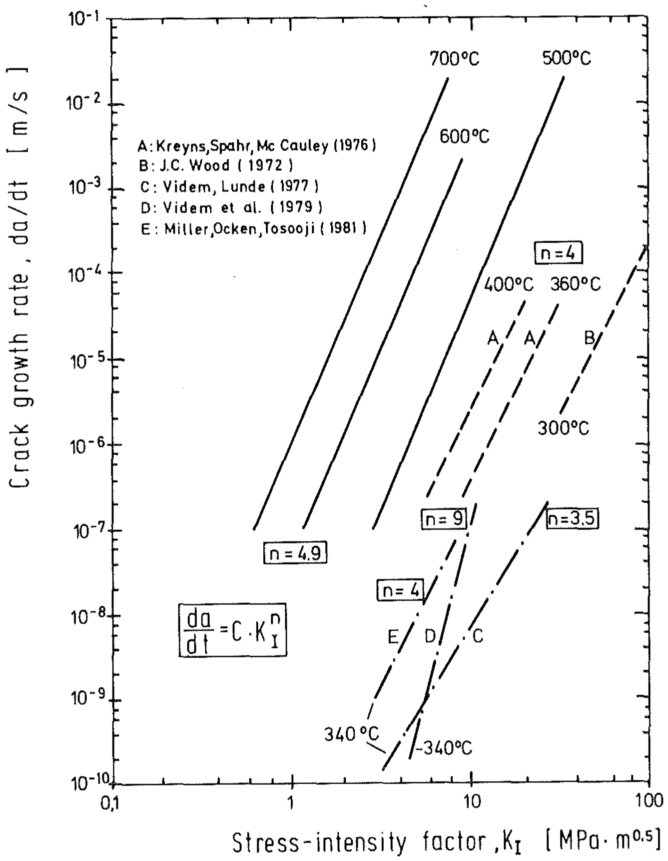


Figure 14: Crack growth rate versus stress-intensity factor for Zircaloy tubing failed due to iodine-induced stress corrosion cracking (comparison with literature data).

300 to 400°C, which underlines the reliability of the model results. The consideration of a plastic zone ahead of the crack tip is probably an important prerequisite for the successful analysis of crack propagation at higher temperatures. Consideration of a separate crack initiation phase also supports the calculation of growth rates of the appropriate order of magnitude /8/.

3.5 Relevance of the SCC Failure Test Results to Transient Fuel Rod Behavior

Iodine can cause low-ductility failure of zircaloy due to SCC over a wide range of temperatures up to about 850^{o}C. But the burst strain is significantly reduced only after a critical iodine concentration (which depends strongly on temperature) has been exceeded. To predict in-pile SCC failure during a LOCA transient, it is therefore important to compare the critical iodine concentration with the estimated iodine concentration in the fuel-cladding gap of an actual fuel rod.

In-pile experiments simulating the second heatup phase of a LOCA were performed in the FR 2 reactor at KfK. The objective of the in-pile tests was to provide information about effects of a nuclear environment on the mechanisms of fuel rod failure under LOCA conditions. The main parameters of the test program were burnup (2500 to 35 000 MWd/t_U) and rod internal pressure (25 to 125 bar). The test procedure and the results obtained are described in references 10 and 11.

An iodine inventory of 2.2 mg/cm^3 in a LWR fuel rod (PWR) was estimated for a burnup of 35 000 MWd/t_U using the assumptions that: (a) the released iodine is homogeneously distributed in the free volume (dishing, gap, and pores), and (b) the iodine release is 10%, which was the maximum value determined for fission gas release during the steady state preirradiation of the FR 2 fuel rods /10,11/. Since, as a first approximation, the iodine release can be assumed to be similar to the overall fission gas release, a 10% release seems reasonable. During a LOCA transient, the additional fission gas release may reach 6% /10,11/.

Comparing the critical iodine concentrations determined from out-of-pile tests with the iodine supply in a fuel rod after a burnup of 35 000 MWd/t_U (2.2 mg/cm^3), it is apparent that an influence of iodine on the burst strain can actually be expected to occur only below 700^{o}C (fig.10). At higher temperatures, the iodine supply in the fuel rod is less than the critical iodine concentration required for iodine-induced SCC of zircaloy cladding (fig.10).

Many incipient cracks (which did not propagate) were detected on the cladding inside surface of the in-pile LOCA-tested fuel rods. This suggests that iodine was not present in sufficient concentration to cause crack propagation. Figure 15 shows results of PIE metallographic examinations of four of the failed high burnup fuel rods. On the cladding inside surface, incipient cracks are apparent similar to those observed in the out-of-pile experiments in which the iodine concentration was too low to cause low-ductility cladding failure. At axial cladding positions where little or no plastic deformation occurred and in test rods with low burnup fuel, no crack formation on the cladding inside surface was evident (fig.15).

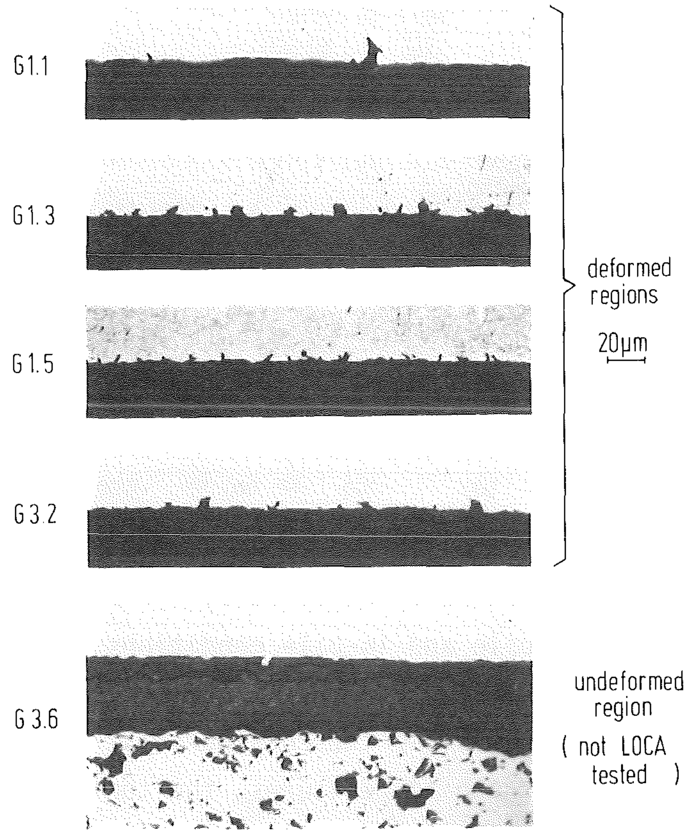


Figure 15: Fuel cladding interfaces of high burnup fuel rods (35 000 MWd/t_U) which failed during an in-pile LOCA transient at temperatures $\geq$ 780^{o}C.

The burst strains of in-pile LOCA-tested fuel rods (both FR 2 and PBF) are plotted versus temperature in figure 16, together with results of laboratory experiments. No influence of iodine on burst strain was observed in the in-pile experiments, i.e., all of the cladding tubes failed in a ductile mode, despite the high burnups reached in some of the fuel rods. However, the burst strains correspond roughly to those of the out-of-pile iodine-containing specimens. The strong reduction in burst strain for the in-pile rods was probably due to large temperature variations along the circumference of the cladding. Low-ductility cladding failures should not have been expected for the LOCA-

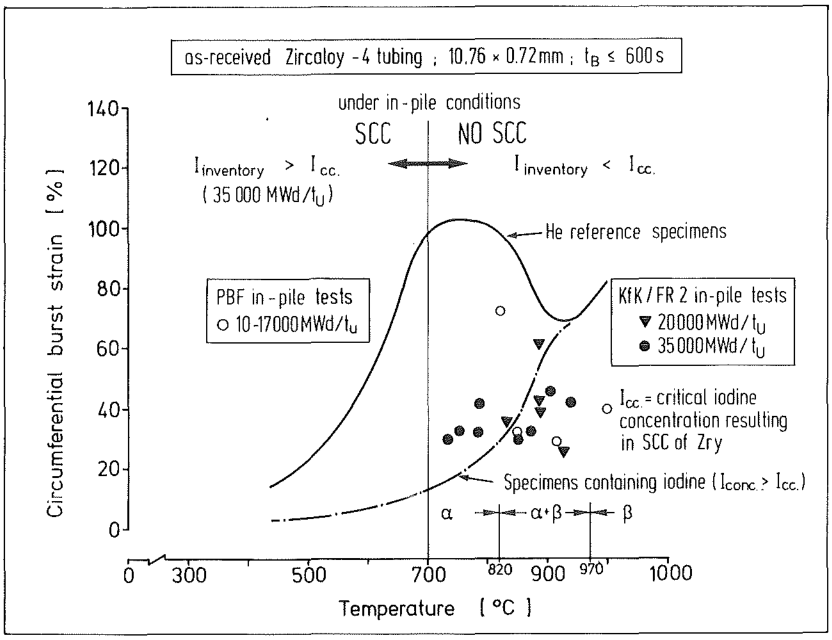


Figure 16: Influence of iodine on burst strain of Zircaloy-4 tubing under out-of-pile and in-pile conditions.

tested high burnup fuel rods since the rods burst at temperatures above 700°C (730 to 900°C). At these temperatures, the iodine concentration required for low-ductility SCC failure is much higher than the estimated iodine supply within the fuel rod (fig.10) /3,4/.

With respect to Anticipated Transients Without Scram (ATWS) which, in principle, are more steep power ramps, an influence of iodine on the mechanical properties of zircaloy cladding is very probable. Mechanical interactions between fuel and cladding would be stronger and the release of fission products distinctly higher in ATWS transients than in less steep operational power ramps due to the higher overall fuel temperatures. In ATWS transients, the anticipated maximum cladding temperatures would, in general, be below 700^{o}C. At these temperatures, the susceptibility of zircaloy to iodine-induced SCC is very high.

4. Major Results and Conclusions

- Out-of-pile creep rupture and burst tests with Zircaloy-4 specimens containing simulated fission products, which were performed between 500 and 900^{o}C, revealed that only iodine can cause low-ductility failure due to SCC. With as-received specimens, the circumferential burst strain was reduced, and with internally preflawed specimens both the burst strain and the time-to-failure were reduced.

- CsI can decompose at rather low oxygen potentials. Under the conditions tested (700^{o}C), Cs-molybdate forms at low oxygen potentials ($\approx$ -400 kJ/mol O_2), resulting in a sufficient iodine activity to cause low-ductility SCC failure of the cladding. The CsI decomposition by the formation of Cs-uranate requires higher oxygen potentials ($\approx$ -220 kJ/mol O_2).

- Iodine can cause low-ductility SCC failure of Zircaloy-4 tubing up to about 850^{o}C. However, the circumferential burst strain is reduced only after a critical iodine concentration (which depends strongly on temperature) has been exceeded.

- The largest reduction in burst strain of as-received tubing due to iodine-induced SCC occurs between 600 and 800^{o}C. At temperatures $\leq$ 550^{o}C, the resulting circumferential burst strains of iodine-containing specimens were $\leq$ 1%, compared to about 20% for the reference specimens.

- The transition from the normal ductile failure mode to the low-ductile ("brittle") failure mode takes place in a very narrow range of iodine concentrations. It is extremely pronounced below 800^{o}C and less so at higher temperatures.

- The critical iodine concentration depends strongly on temperature but is independent of burst pressures in the range examined, which resulted in time-to-failures $\leq$ 3600 s. The critical iodine concentration varies between 0.01 mg/cm^3 at 500^{o}C and 50 mg/cm^3 at 900^{o}C.

- Thin oxide layers on the inner cladding surface and/or the presence of UO_2 influence the critical iodine concentration values. Whereas thin oxide layers result in a decrease of the critical iodine concentration, the presence of UO_2 fuel results in an increase.

- Elemental iodine reacts completely with zircaloy to form gaseous zirconium tetraiodide (ZrI_4) and various condensed zirconium iodides (ZrI_x) at all temperatures examined (500 to 900^{o}C). The amount and chemical composition of the solid ZrI_x phases depends on the initial iodine concentration and temperature.

- Iodine-induced SCC failure of zircaloy cladding is caused by gaseous ZrI_4, the predominant gas phase in the system. In the absence of an iodine-containing gas such as ZrI_4, no SCC failure of the Zircaloy-4 tubing occurs. That is, SCC behavior is directly related to the ZrI_4 partial pressure.

- The onset of SCC occurs within a rather broad range of ZrI_4 pressures. However, an upper limit for the ZrI_4 pressure exists above which SCC failure of zircaloy always occurs. This critical ZrI_4 pressure varies between 5 mbar at 550^{o}C and 43 mbar at 800^{o}C.

- The plot of critical iodine concentration versus reciprocal temperature shows that the different portions of the curve have different slopes. Extrapolation of the data is therefore difficult. However, if the estimated actual ZrI_4 gas pressure in the tube specimens is plotted versus 1/T, the high temperature data can be extrapolated to low temperatures. For this reason, it appears to be more appropriate for SCC assessment to consider the critical ZrI_4 pressure rather than the initial iodine concentration.

- SCC failure of zircaloy occurs by a gas adsoprtion process. Only iodine-containing gas species are responsible for crack initiation and crack propagation. The rate-controlling step for crack propagation is probably the gaseous diffusion of iodine or iodine-bearing gas to the crack tip where chemisorption occurs.

- The iodine-induced low-ductility failure behavior of zircaloy tubing can be described by fracture mechanics methods. A modified version of the stress-intensity factor K_I-concept of LEFM can be used to predict times-to-failure. SCC growth under static loading conditions obeys a power law of the form $da/dt = C(T) \cdot K^n_{I,eff}$. A plastic region in front of the crack tip, which effectively increases the crack depth, and the continuous change in crack geometry are considered. C(T) is an exponential function of temperature with an activation energy of $2.39 \cdot 10^5$ J/mol between 500 and 600°C, and the exponent n is 4.9 for all temperatures (500 to 700°C).

- The type of fracture depends on temperature. At 500°C the cracks were primarily transgranular to a depth of 40 to 60% of the wall thickness before ductile rupture occurred. At 600°C the crack were initially intergranular, followed by a transgranular region to a depth of 75 to 90% of the wall thickness before ductile rupture occured. At 700°C and higher the cracks were almost always completely intergranular with no pronounced ductile rupture.

- A comparison of the critical iodine concentration determined out-of-pile with the iodine inventory in an actual fuel rod after a burnup of 35 000 MWd/t_U (2.2 mg/cm^3) shows that iodine can be expected to influence burst strain only at temperatures < 700°C.

- In the FR 2 in-pile LOCA tests, no influence of fission products on the deformation behavior of zircaloy cladding has been observed, even in high burnup fuel rods (35 000 MWd/t_U). However, in these experiments, the cladding burst temperature varied between 730 and 900°C where the expected iodine supply is less than the iodine concentration required for SCC failure.

- With respect to ATWS transients, an influence of iodine on the mechanical properties of zircaloy is more likely than in LOCA transients, since the maximum cladding temperatures would, in general, be below 700^{o}C.

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