KfK 3054
September 1980

Influence of Simulated Fission Products on the Ductility and Time-to-failure of Zircaloy-4 Tubes in LWR Transients

P. Hofmann, J. Spino
Institut für Material- und Festkörperforschung
Projekt Nukleare Sicherheit

Kernforschungszentrum Karlsruhe

KERNFORSCHUNGSZENTRUM KARLSRUHE

Institut für Material- und Festkörperforschung
Projekt Nukleare Sicherheit

KfK 3054

Influence of simulated fission products on the ductility and time-to-failure of Zircaloy-4 tubes in LWR transients*

P. Hofmann, J. Spino

* Paper presented at the CSNI Specialist Meeting on "SAFETY ASPECTS OF FUEL BEHAVIOUR IN OFF NORMAL AND ACCIDENT CONDITIONS", 1st - 4th September 1980, Espoo, Helsinki, Finland

Kernforschungszentrum Karlsruhe GmbH, Karlsruhe

Kernforschungszentrum Karlsruhe GmbH
ISSN 0303-4003

Influence of simulated fission products on the ductility and time-to-failure of zircaloy-4 tubes in LWR transients

Summary

The compatibility behavior of simulated fission product elements as well as compounds with Zircaloy-4 was studied in the temperature range of 500 to 1000°C. Also tube burst experiments were performed with these substances in order to determine their influence on the mechanical properties of Zircaloy for transients under LWR accident conditions. The test results have shown that there is a more or less distinct change in burst strain and time-to-failure with all the substances investigated as compared to the fission product free reference specimens. However, only iodine or volatile iodine compounds result in low ductility failure of Zircaloy-4 cladding tubes up to about 800°C. By contrast, CsI does not exert an influence at all. Selenium and tellurium give rise to chemical interactions with the Zircaloy, partly leading to a reduction of burst strain. The critical iodine concentration resulting in stress corrosion cracking of Zircaloy-3 was determined as a function of temperature.

Einfluß von simulierten Spaltprodukten auf die Duktilität und Standzeit von Zircaloy-4-Hüllrohren unter LWR-Störfallbedingungen

Zusammenfassung

Es wurde das Verträglichkeitsverhalten von simulierten Spaltproduktelementen und -verbindungen gegenüber Zircaloy-4 im Temperaturbereich zwischen 500 und 1000°C untersucht. Mit diesen Substanzen wurden auch Rohrberstexperimente durchgeführt, um deren Einfluß auf die mechanischen Eigenschaften des Zircaloy bei Störfalltransienten zu ermitteln. Die Versuchsergebnisse zeigen, daß es in Verbindung mit allen untersuchten Substanzen zu einer mehr oder weniger ausgeprägten Änderung der Berstdehnung und Standzeit gegenüber den spaltproduktfreien Referenzproben kommt. Jedoch nur Jod oder leicht flüchtige Jodverbindungen bewirken ein verformungsarmes Versagen der Zircaloy-4-Hüllrohre bis etwa 800°C. CsI besitzt dagegen keinen Einfluß. Selen und Tellur verursachen chemische Wechselwirkungen mit dem Zircaloy, wodurch es z.T. zu einer Abnahme der Berstdehnung kommt. Es wurde darüberhinaus die kritische Jodkonzentration in Abhängigkeit der Temperatur bestimmt, die zur Spannungsrißkorrosion des Zircaloy-4 führt.

CONTENT

		page
1.	Introduction	1
2.	Definition of the problem	1
3.	Experimental procedure	2
4.	Experimental results	3
4.1	Chemical interactions between simulated fission products and Zircaloy-4	3
4.2	Burst experiments and creep rupture tests	3
4.2.1	Time-to-failure	3
4.2.2	Burst strain	4
4.2.3	Evaluation of the fission products	4
4.3	Determination of the critical iodine concentration	4
4.4	Metallography, fractography	5
5.	Discussion	6
6.	Conclusions	9
7.	Acknowledgements	9
8.	References	10

1. INTRODUCTION

The fuel element of a nuclear reactor undergoes various chemical and mechanical loads during normal operation and, above all, in transients under accident conditions. In the course of nuclear fission of UO_2 some 30 different fission product elements are formed, and oxygen is released. Part of the fission products are volatile and will therefore escape from the fuel during irradiation. The fission product elements which are not stable thermodynamically with Zircaloy-4 cladding material, are susceptible of reacting with the cladding material; so does UO_2 /1/. Besides, with increasing burnup, the gap provided between the fuel and the cladding material will narrow as a result of cladding creepdown, fuel swelling and relocation, and it will ultimately disappear. Then, in addition to chemical interactions,there will be mechanical pellet-cladding interactions (PCI). The mechanical interactions are evident,particularly, when the reactor power is increased because the fuel exhibits more thermal expansion than the cladding material. Moreover, in transients under accident conditions, the cladding material temperature is increased. For reasons of safety it is therefore of great importance to know how the Zircaloy-4 cladding material behaves under the combined chemical and mechanical loads occuring during power increases and transients under accident conditions.

2. DEFINITION OF THE PROBLEM

Extensive studies have been made during recent years on the fuel rod behavior under normal reactor operation and during power ramps. The results obtained until 1977 have been delineated in detail in a state-of-the-technology review of fuel cladding interactions /2/. More recent results available in this field were presented at various conferences/3,4,5,6/. It was demonstrated without any doubt that the fuel element failure during fast power ramps is mainly due to stress corrosion cracking (SCC).Iodine is considered to be the reactive fission product element /2,3,4,5,6,8,9/ although in out-of-pile ingestigations also Cd and Cs gave rise to Zircaloy-4 embrittlement /10,21,23,24/. However, SCC failures of the cladding material will occur only after a certain burnup since both the fission product concentration and the mechanical interactions depend on the burnup. Moreover, a certain critical rod power must be exceeded /7,8/. In case of rather slow power increases, damage to the fuel rods can be avoided /7,8/. Also use of a PCI resistant fuel or cladding will improve the fuel rod behavior with respect to SCC failures /9/.

This situation in mind, when investigating the fuel rod behavior during LWR transients (ATWS, LOCA, RIA, PCM) *, the question must be solved which influence is exerted by the fuel and the fission products on the mechanical properties of Zircaloy-4 under the particular conditions concerned. An accelerated chemical attack of the cladding must be anticipated on the basis of the partly high cladding material temperatures which are supposed to exist in transients under accident conditions. At the same time, the cladding tube undergoes great mechanical stresses. The tangential tensile stress on the fuel rod cladding tubes is brought about by mechanical interaction between the fuel and the cladding material (PCI) in ATWS and RIA transients and during LOCA transients by the inner gas pressure (filling gas, fission gas) rising with the temperature while the external pressure of the coolant (system pressure) decreases simultaneously. In PCM accident, the cladding tube collapses onto the fuel since the external pressure is greater than the inner pressure and it has to sustain compressive stresses.

In all transients considered here, an additional release of volatile fission products must be expected on account of a great increase in fuel temperature; but the rate of release will be the smallest in a LOCA transient because of the temperature distribution in the UO_2 and the low average temperature /11/.

In studies of the fuel rod behavior during a LOCA it was demonstrated by extensive out-of-pile burst and creep rupture tests involving iodine that up to about 800°C SCC can lead to low ductility failure of the Zircaloy-4 cladding tube /15,16,17/. Moreover, the time-to-failure is in some cases reduced to a high extent by the in-

---

* ATWS: Anticipated Transients Without Scram; LOCA: Loss-of-Coolant Accident; RIA: Reactivity Insertion Accident; PCM: Power-Cooling Mismatch Transient.

fluence of iodine. However, the critical iodine concentration leading to SCC failures of Zircaloy tubing remains to be determined as a function of temperature.

It was shown in previous out-of-pile investigations with UO_2 of different O/U-ratios that in LOCA transients the oxygen potential of UO_2 only has a negligible influence on the mechanical properties of Zircaloy-4 /12/. The oxygen transport from UO_2 to Zircaloy, and hence the embrittlement of the latter, is very small. The same applies to ATWS transients. In the case of PCM transients however, where temperatures up to 1500°C can be reached, greater chemical interactions between the fuel and the cladding material take place above 1000°C on account of the good solid contact between UO_2 and Zircaloy. In PCM-transients the embrittlement of the inner side of the cladding material by UO_2 corresponds approximately to the embrittlement on the external side by steam /13,14/.

It was the purpose of this work to examine which other fission products or fission product compounds besides iodine react likewise with Zircaloy-4. Therefore, tube burst experiments were performed with the substances having proved aggressive towards Zircaloy in order to determine their influence on burst strain and time-to-failure of the cladding tubes under LWR transient conditions. Moreover, the critical iodine concentration above which low ductility failure of the Zircaloy cladding tube due to SCC will occur was determined as a function of temperature. All experiments were performed under the German Nuclear Safety Project (PNS).

3. EXPERIMENTAL PROCEDURE

The out-of-pile experiments were made on non-irradiated Zircaloy-4 tube specimens (10.76 x 0.72 mm; 60-600 mm length) mainly under inert gas. Part of the experiments were made in steam /19,20/. The test specimens were heated under inert gas by means of thermal radiation and in steam by means of a central heater (fuel rod simulator). The cladding tubes were subjected to mechanical loading by gas pressure (helium) within the specimens. The test equipment and the experimental procedure have been described elsewhere /14,15,16,17,19/.

Both,creep rupture tests as well as temperature and pressure transient burst test were performed. The burst temperatures varied between 600 and 1000°C. During the tests, the pressure in the specimens and the cladding material temperatures were measured continuously. Besides, also cladding tube ballooning as a function of time was measured in some tests /19,20/. The cladding material was used in the as-received condition, preoxidized, and predamaged (100 µm deep internal notches). The test specimens were filled with simulated fission products, closed and welded in gloveboxes in a highly pure inert gas atmosphere.

Also isothermal compatibility annealings at 500, 700, 900 and 1100°C were made with Zircaloy and the substances indicated below. The annealing time varied between 600 and 6000 s. The elements and compounds were annealed in small crucibles made of Zircaloy-4 which were gas-tight sealed /22/.

The following simulated fission product elements and compounds were investigated:

- Se, Mo, Cd, Sn, Sb, Te, I, Cs;
- TeO_2, TeI_4, $ZrTe_2$, ZrI_4, I_2O_5, Cs_2O, Cs_2Te, CsI;
- Cs_2ZrO_3, Cs_2MoO_4.

The simulated fission product concentration varied,in general,between 30 and 350 mg per 1 cm of tube length (1 cm corresponds roughly to 2.9 cm^2 of inner cladding tube surface or 0.68 cm^3). These concentrations do imply, partly, high burnup fission product yields and/or fission product release rates. In the particular case of iodine, initial concentrations as low as 0.007 mg per cm tube length were employed.

After the tests, the tube burst specimens were investigated metallographically and by scanning electron microscopy (SEM). The compatibility specimens were likewise subjected to metallographic tests and to tests using a microprobe analyser and SEM. Some of the reaction products formed were also analyzed chemically.

The "embrittlement" of Zircaloy-4 was determined by comparing the results in test environments with those found in an inert environment (He) in terms of burst strain, time-to-failure, and fracture surface structure. The term embrittlement is used simply to denote a reduction of ductiliy, and is not intended to imply that the fracture process necessarily occurs in a completely brittle mode.

4. EXPERIMENTAL RESULTS

4.1 CHEMICAL INTERACTIONS BETWEEN SIMULATED FISSION PRODUCTS AND ZIRCALOY-4

The investigations of chemical interactions between simulated fission product elements and compounds with Zircaloy-4 cladding material yielded the following results /22/:

- No chemical interactions with Zircaloy-4 were caused by Mo, Cs and CsI, not even at the maximum temperature investigated (1100°C/6000s). A slight increase in hardness of the Zircaloy down to a depth of 100 µm at the maximum was found in the compatibility annealings with Mo. The increase in hardness is very probably due to the oxygen uptake by Zircaloy. The oxygen is present in the Mo powder (0.32 wt.%) as an impurity.
- Oxygen diffused into Zircaloy forming an oxygen stabilized α-Zr(O) phase during annealings with the oxide compounds Cs_2O, I_2O_5, Cs_2ZrO_3 and Cs_2MoO_4 which resulted in some embrittlement of Zircaloy. However, a noticeable uptake of oxygen by Zircaloy takes place only from 700°C on. At 1100°C/6000 s, the depth of the α-Zr(O) phase varied between 60 µm (Cs_2ZrO_3) and approx. 200 µm (Cs_2MoO_4).
- Se, Te, Sn, Sb and iodine caused a nearly uniform attack of the Zircaloy. In all cases, these elements do not diffuse into the cladding material but the cladding material gets dissolved by the elements, while partly forming compounds such as $ZrSe_2$, $Zr_{1-x}Te$, $ZrSn_2$ and Zr_3Sn_2 (at elevated temperatures). The reaction products produced by iodine were not completely identified because of their hygroscopic nature, but the formation of gaseous ZrI_4 and a certain amount of condensed lower iodides, can be assumed.
- Attacks on the grain boundaries were caused by Cd, Cs_2Te and TeI_4. Visible reactions of Cd with the Zircaloy take place only above 700°C. Cd diffuse into Zircaloy along grain boundaries and destroys the grain structure, while partly forming $ZrCd_2$. At 700°C and above, Cs_2Te reacts with Zircaloy uniformly on the circumference of the test specimens. From 900°C on, also stronger attacks of the cladding material take place locally along grain boundaries. TeI_4, which decays into Te, I_2 and TeI_2 above approx. 300°C, reacts with Zircaloy-4 already at 500°C, preferably along grain boundaries.

In brief, the results of the compatibility study is that with the exception of Mo, Cs and CsI, chemical interactions take place with Zircaloy-4 cladding material in the presence of the substances investigated. Therefore, it is interesting to know to which extent the mechanical properties of Zircaloy will change by these reactions. The results of the burst experiments with tube specimens containing little amounts of the reactive simulated fission product elements and compounds will be delineated in the following chapter. It should be added that in the tube burst tests the concentration of the reactive fission products was clearly lower than in the compatibility tests. The purpose was to simulate conditions relevant to practical application.

4.2 BURST EXPERIMENTS AND CREEP RUPTURE TESTS

The test results of the burst and creep rupture tests with Zircaloy tube specimens containing little amounts of simulated fission product elements or compounds, are represented in Figs. 1 to 3. The figures show circumferential burst strain versus time-to-failure for the different types of tube specimens (as-received, notched) and chemical substances investigated. The changes of burst strain and time-to-failure of the fission product containing tube specimens were determined by comparing their burst data with those of the fission product free reference specimens. Some of the data on reference specimens and on fission product containing specimens have been confirmed repeatedly; the scatter in the burst data is small.

4.2.1 TIME TO FAILURE

In the temperature and pressure transient experiments the tube specimens were exposed to an internal helium pressure of 70 bar at $20^{o}C$ and subsequently heated until bursting. The average heating rate ($T_{20^{o}C} \rightarrow T_{burst}$) was about $9^{o}C/s$. During the heating process, a pressure rise takes place in the tube specimens. The burst pressures varied therefore between 80 and 111 bar, the burst temperatures between 730 and $805^{o}C$, and the times-to-failure between 70 s ($ZrTe_2$) and about 105 s (Cs_2ZrO_3). The oxides (Cs_2O, Cs_2MoO_4, Cs_2ZrO_3, TeO_2) cause an increase in time-to-failure as compared to the reference specimens (Fig.1).

In the isothermal-isobaric experiments a constant pressure of 75 bar was applied after the temperature of $700^{o}C$ had been reached; this pressure corresponds also to the burst pressure. The times-to-failure varied for the as-received cladding tubes between 588 s (I_2O_5) and 850 s (Cs_2MoO_4) (Fig.2), and for the predamaged cladding tubes between 14 s (I_2O_5) and 917 s (Cs_2MoO_4) (Fig.3). It can be seen from these data that, especially on the internally notched specimens, the time-to-failure is greatly reduced by the presence of iodine or the highly volatile iodine compounds (I_2O_5, TeI_4, ZrI_4) (Fig.2), but not with the specimens in the as-received condition (Fig.3).

4.2.2 BURST STRAIN

As to the burst strains, it can be recognized that they are more or less influenced by all substances investigated. However, only in combination with elemental iodine or with the volatile iodine compounds (I_2O_5, ZrI_4, TeI_4) all types of specimens in creep rupture and burst experiments exhibit a marked reduction in burst strain, which is especially great in the case of predamaged cladding tubes (Figs.1, 2, 3). Generally, the burst strains of these specimens are less than 35% and even below 5% in the case of notched specimens (Fig.3). In some cases, also Se caused a low ductility failure of the Zircaloy-4 tubing (Fig.2).

4.2.3 EVALUATION OF THE FISSION PRODUCTS

As already mentioned iodine as well as I_2O_5, ZrI_4 and TeI_4 always lead to a great reduction in burst strain, partly also in time-to-failure. By contrast, CsI did not exert any influence on the mechanical properties of Zircaloy, not even if it was present in high concentrations. Selenium showed a partial influence on burst strain. The creep rupture tests with the selenium containing tube specimens in the as-received condition yielded a low ductility failure of the cladding tubes (Fig.2; about 40% as compared with 120% of the reference specimens). This influence of selenium was not found in notched specimens and in transient experiments, although the experiments were performed repeatedly under the same boundary conditions (Fig.1, 3). Compared with the other substances, tellurium has also shown a small influence on burst strain; however, not as clearly pronounced as iodine and also less pronounced than selenium (Fig.3). Cd and Mo, which in the uniaxial tensile tests caused high embrittlement of Zircaloy /10,21,23,24/, did not reveal any considerable effect on the mechanical properties of Zircaloy-4 tubing in these experiments.

4.3 DETERMINATION OF THE CRITICAL IODINE CONCENTRATION

The burst experiments described before, which utilized a multitude of simulated fission product elements and compounds, have shown that it is mainly iodine that influences the burst strain. It also influences in some cases the time-to-failure of the Zircaloy-4 cladding tubes. Since in these experiments the concentration of fission products inside the tube specimens was relatively high, it was important to know how the change of the ductility depends on the iodine concentration.

Of particular interest was the discovery of the iodine concentration (in advance called "critical") for which a strong reduction of the burst strain occurs as a consequence of SCC. This critical concentration was expected to be highly dependent on temperature and therefore extensive experiments were conducted on as-received Zircaloy-4 tubing in the temperature range between $600^{o}C$ and $1000^{o}C$ under helium.

Isothermal-isobaric creep rupture tests were preferred for this purpose to transient burst tests, since the control of test parameters like temperature, heating time, burst pressure and time-to-rupture, is more properly achieved in the first type of experiments. Moreover, to assure the reproducibility of the results it was necessary to preserve during the experiments as much as possible of the initial iodine amounts inside the specimens. This was reasonably achieved by means of a thin zirconium membrane (about 0.1 mm thick) which, welded at the pressure inlet orifice of each sample, avoided the escape of volatile reaction product (i.e. ZrI_4 (g)) during the heat-up period (about 1000 sec) in absence of an applied gas pressure. Burst pressures ranging between 20 and 200 bar were used in order to provide comparable times-to-rupture (60-240 sec) for all the temperatures checked. The initial iodine concentrations were varied between 0.01 and 100 mg/cm^3 (1 cm^3 is equivalent to 4.29 cm^2 of tube inner surface or 1.47 cm of tube length).

The presentation of the burst strain, for a given temperature, as a function of the initial iodine concentration clearly shows the existence of a particular range of iodine concentration within which the ductility of the Zircaloy tubes is sensibly reduced. A low level value for the burst strain is rapidly obtained after the critical range is exceeded (Fig.4). This critical iodine range moves to higher values as the temperature increases (Fig.4). The jump from the normal ductile failure of the Zircaloy to the low ductility failure mode was found to be extremely pronounced at low temperatures (600°C-750°C), becoming smoother at higher temperatures (750°C-900°C). A tendency to a gradual disappearence of iodine SCC of Zircaloy tubing is therefore noticeable while the temperature increases. This can also be recognized by the absolute difference of the burst strains at both sides of the critical iodine concentration range, which starts to decrease at 800°C and becomes negligible above 900°C.

Further evaluation of the data demanded a more precise definition for the critical iodine concentration, especially for temperatures above 750°C. The location of the steepest part of the curve representing burst strain versus iodine concentration (Fig.4) was used as a criterium for determining the critical values. Concentrations selected in that way showed a good correlation if plotted as a function of the reciprocal temperatures. The corresponding Arrhenius plot (Fig.5) shows that SCC of Zircaloy can be attributed to the same type of chemical process between 900°C and 700°C. On the other hand, the misalignment of the point belonging to 600°C, one fo the experimental data points with a great degree of confidence, manifests that a sensible change in the corrosion mechanism takes place between 600°C and 700°C.

This gives a good reason not to consider the extrapolation of the data from high ($\geq$ 700°C) to low temperatures, especially to the zone corresponding to the "normal reactor operation". In this region (300°C-400°C) a great variation in the literature data exists /33-41/, partly due to difference in the materials used, types of tests, the definition of the critical iodine concentration, and test parameters.

4.4 METALLOGRAPHY, FRACTOGRAPHY

The metallographic and SEM examinations clearly show the impact of iodine on the chemical/mechanical behavior of Zircaloy-4 during the experiments. In tube specimens containing no iodine at all or only very little amounts of it normal plastic behavior is observed which means that the Zircaloy tube gets very much deformed (80-120%) while its wall thickness decreases continuously. Following very great strains a local necking appears which results in a ductile failure of the cladding tube. The ductile shear fracture occurs at an angle of about 45° (Fig.6). Above the critical iodine concentration the tubes fail after slight deformations already. Zircaloy undergoes failure as a result of iodine SCC. The fracture occurs normal to the direction of the applied load, practically in the absence of any local necking of the cladding tube (Fig.6). The same deformation and fracture behavior is observed with specimens predamaged internally.

If one examines the burst tube specimens under the scanning electron microscope (SEM) one recognizes that due to iodine a great number of incipient cracks of different sizes are formed on the inner surface (Fig.7). These incipient cracks can be observed over the entire circumference and specimen length. All of them run in the axial direction, i.e., parallel to the tube axis. The cracks penetrate into the cladding material which means that the stress immediately below the tip of the crack and in the remaining cladding tube cross section rises continuously. As soon as a critical crack depth is attained, the ultimate tensile strength of the Zircaloy is reached and an instantaneous fracture of the tube occurs. It can be clearly seen from the fracture surface that the type of crack caused by iodine is mainly intergranular; the spontaneous fracture of the remaining cladding wall is a ductile one (Fig.7). The intergranular type of crack can be recognized also in the transverse crossection of the failed tubes (Fig.6).

In the course of experiments involving iodine concentrations below the threshold value only very small single intergranular incipient cracks can be detected on the cladding tube inner surface (Fig.8). The amount of iodine is no longer sufficient to form the respective reaction or adsorption layers at the tip of the cracks. Fracture of the cladding tubes then occurs exclusively in a ductile mode (Fig.8).

A further characteristic of the critical iodine concentration range is that specimens initially charged with iodine concentrations within this range, change their fracture mode from "ductile" (Fig.8) to "brittle" (Fig,7) in going from the low concentration side of the range to the high concentration side. Furthermore, as a confirmation of the tendency of SCC to disappear at high temperatures, no net brittle fractures were observed in fractographs for 850^{o}C and above, even for specimens placed far inside the low strain zone that means with high initial iodine concentrations.

SEM examination of burst tube specimens containing other fission products than iodine reveal only ductile fracture surfaces except for Se and Te. In Zircaloy tubings filled with Se or Te, intergranular incipient cracks were observed in the wall below surface reaction layers (Fig.9). The intergranular type of crack, however, cannot always be clearly distinguished due to a very thick coating on the internal cladding and the fracture surface (Fig.9). But only in the case of the as-received tube specimens containing Se the intergranular cracks penetrated very deep into the cladding wall (Fig.9) which resulted in a low ductility failure. The fractography of the specimens which contained Cd showed an entirely ductile mode of failure. The same holds for all the other examined burst specimens.

5. DISCUSSION

The compatibility tests have shown that except for Cs, CsI and Mo the simulated fission product elements and compounds investigated prove to be aggressive against Zircaloy-4 at high temperatures. The most serious attack on Zircaloy was caused by iodine, to a lesser degree by selenium, tellurium and cadmium,in this order. Also in the case of a combined chemical, mechanical loading of Zircaloy-4 tubes, iodine caused the greatest change in mechanical properties, likewise to lesser degrees by selenium and tellurium. The effect of selenium and tellurium, however, is not so uniform as that of iodine, which means that burst strain was not reduced in all cases. The reasons for this behavior remain to be elucidated.

The effect of embrittlement of Zircaloy by Cd /10,21,23/ and Mo /24/ as described in the literature could not be confirmed. As to the effect of cadmium, it can be imagined that the mechanism of liquid metal embrittlement of Zircaloy is no longer effective at the high temperatures applied here. The experiments described in the literature /10,21,23/ were performed at 300-350^{o}C. However, it is also possible that the relatively high oxygen content of the Cd used in our experiments (about 3 wt.%) is responsible for this phenomenon. The high oxygen content could also be a reason for the fact that Cd reacted with the Zircaloy from 700^{o}C on only. After the compatibility annealings performed at 500^{o}C, Cd was still present as a powder although the melting point of Cd lies at about 320^{o}C. By contrast, Cd oxide does not melt below 1200^{o}C. Starting at 700^{o}C, a reduction of Cd oxide by Zircaloy becomes probable for reasons of kinetics. The metallic Cd so formed can then react with the Zircaloy.

The highly embrittling effect of Mo on Zircaloy as described in /24/ is very probably caused by oxygen impurities present in the Mo powder (oxygen analyses of Mo were not described).

On the basis of thermodynamic considerations, I, Se and Te should be bound in the fuel rod by Cs forming CsI, Cs_2Se, and Cs_2Te. These compounds, however, are either no longer reactive at all with respect to Zircaloy (CsI), or they react much less violently than the elements (Cs_2Se, Cs_2Te). At any rate, they do no longer exert an influence on the mechanical properties of Zircaloy in the case of simulated LOCA transients (Figs.1, 2, 3).

Despite the fact that CsI cannot cause SCC failure of the Zircaloy cladding in out-of-pile experiments, this mechanism of failure is observed in in-pile experiments. There are several explanations for this fact, but none of them has been proven in an unambiguous way. It is conceivable that possibly available CsI is split up under certain conditions. Two mechanism have so far been described in the literature for CsI splitting /25,26/; however, their efficiency is not sufficiently known. For instance, it was demonstrated that CsI is capable of disintegration in the γ-radiation field /25/ and that it is susceptible of being split by a high oxygen potential while forming Cs-oxides /26/. However, it has not been demonstrated so far whether the CsI splitting by these mechanisms is sufficiently strong to cause the observed effects (SCC by iodine). Own preliminary out-of-pile experiments with CsI, conducted with different oxygen potentials, have shown that CsI splitting can take place at such a fast rate that even in transient burst experiments the Zircaloy cladding fails as a result of SCC. This means low ductility failure of Zircaloy-4 similar to that with elemental iodine. Now, it must be proven whether such oxygen potentials can occur temporarily in the fuel rod during fast power ramps and reactor transients. Relevant studies are under way.
Moreover, there are great differences between the iodine concentration determined out-of-pile resulting in a low ductility failure of the cladding tube due to SCC, on the one hand, and the iodine concentration to be expected on the cladding tube inner surface, on the other hand /28,29/. The iodine supply is much smaller than the demand, both at power ramps and in transients under accident conditions. Nevertheless, the Zircaloy cladding tube may fail in in-pile ramp experiments as a result of PCI/SCC if fuel rods with medium and high burnups and excessive power ramps are involved. This was demonstrated beyond any doubt /2,3,4,5,6/. Therefore, processes must take place in a fuel rod which, during a transient, lead to an elevated iodine concentration at the inner surface, independent of the splitting mechanisms for CsI as described above. This can be achieved only by increased fission product release during a transient or by local, high fission product enrichment during steady state irradiation due to fission product redistribution (e.g., at the UO_2 pellet interfaces). Iodine and cesium enrichments at the pellet interfaces were surely detected /30/. Moreover, it is known that appropriate power ramps will imply crack formation in UO_2, thus releasing spontaneously volatile fission products. These events can give rise to local fission product concentrations at the cladding tube inner surface which are clearly higher than those corresponding to the state of nominal burnup of the fuel. Therefore, when estimating the possible iodine concentration in the fuel rod, one should not assume a homogeneous distribution of iodine. On the other hand, local fission product enrichment cannot yet be quantified /30/.

If one compares the out-of-pile determined critical iodine concentrations with the iodine supply in a fuel rod, e.g., after a burnup of 35 000 MWd/t, it can be recognized that an influence of iodine on burst strain can actually be expected to occur only in the temperature range of 600 to 700°C. Only in this temperature range the iodine supply in the fuel rod is higher than the critical iodine concentration required (Figs.4, 5). However, it must be considered in this comparison that the value indicated for the iodine supply in the fuel rod after 35 000 MWd/t of burnup (2.23 mg/cm^3) would be available on the cladding material surface only in case of complete iodine release. This assumption is certainly not correct. Measurements of the fission gas release after LOCA transients, which can be considered likewise as a measure of iodine release, yielded maximum values of about 6% /11,31/. A comparison of these release rates with the critical iodine concentration assuming a homogeneous distribution of iodine yields too low values. But, as described above, one can expect local enrichments of iodine in fuel rods.

From considerations made in analogy with ramp experiments in which failure by embrittlement of Zircaloy due to PCI/SCC can occur, it had to be expected that similar failure mechanisms can also take place in LOCA transients. It was clearly shown in the out-of-pile experiments that the effect of iodine can imply low ductility failure of Zircaloy cladding tubes up to about 800°C. The burst strains of the cladding tubes are much lower at a sufficiently high idine concentration than that of iodine free reference specimens (Fig.4). A great part of the results was published in /15,16,17,18/.

However, the in-pile LOCA experiments performed so far at the FR 2 (Karlsruhe) and the PBF (Idaho Falls) have not yet furnished a clear indication for the fact that iodine or other volatile fission products exert an influence on burst strain /27, 31,42/. Even with fuel rods of high burnups (35 000 MWd/t). But, in these in-pile LOCA experiments the burst temperature of the cladding tube was always above 700°C. However, at burst temperatures above 750°C the iodine supply on the cladding tube inner surface is too low to cause SCC of Zircaloy, even in the cases where all of the iodine is released (Fig.4). This could be one of the reasons why low-ductility failure of the Zircaloy cladding tube has not yet been observed during in-pile LOCA experiments. In all cases a ductile failure of the cladding tubes occured /27,42/.

This in-pile fuel rod behavior during a LOCA transient can have different causes:

(a) The most trivial reason could be, as already mentioned, that iodine is not present at a sufficiently high concentration on the cladding tube inner surface. Local enrichments in iodine on the cladding tube inner surface are less probable in LOCA transients than in experiments involving power ramps (or in ATWS transients). During a LOCA transient the cladding gets detached from the fuel and an annular space is generated in which the volatile fission products may spread uniformly. This results in a decrease of the specific fission product concentration at the cladding tube inner surface.

(b) Another reason could be that the fuel/fission product chemistry in the fuel rods is no longer relevant to practical application due to the long period between preirradiation and the LOCA experiments. The fuel rods are not preconditioned for a longer time prior to the LOCA transient.Therefore, there is no buildup of short-lived fission products and the fission product chemistry in the fuel rod has not reached its steady-state. (for this reason the fuel rods are preconditioned in the ramp experiments over 300-500 hours in order to build up a steady-state fuel/fission product chemistry).

(c) The LOCA transient in the FR 2 reactor takes a different course than in an anticipated "real" LOCA transient. One does not start the experiment from full rod power ending in the transient, but from a very low rod power (45 W/cm), which is to simulate the decay heat of the fission products only. By this fact the temperature distribution in UO_2 takes a different course in terms of time which might influence the release of fission products.

(d) The fuel rods are opened after preirradiation in order to connect them with pressure transducers. During this step air and humidity might penetrate into the fuel rod which exerts an influence on the chemical state of the fission products and with that possibly on the SCC behavior. Moreover, volatile fission products might escape(for example, the fuel rods to be subjected to power ramps are not opened for instrumentation).

Therefore, considering the items discussed above, a final judgement cannot yet be given on the fission product influence on burst strain of the cladding tubes in a LOCA transient (in-pile). It cannot be excluded that low ductility failure of cladding tubes will result from appropriate preconditioning relevant to service conditions. But, a low ductility failure can be expected with great probability only at burst temperature of the Zircaloy tubing between 600 and 700°C. No in-pile LOCA experiment were performed up to now in this temperature range.

As regards ATWS transients which, in principle, are more intensive power ramps, an influence of the fission products on the mechanical properties of Zircaloy cladding tubes is very probable. Both the mechanical interactions between the fuel and the cladding material and the release of fission products will be distinctly higher in ATWS transients than in power ramps. The same applies to RIA transients. In ATWS transients the anticipated maximum cladding material temperatures will be in generall below 700°C.

Although determinations of critical iodine concentrations are still lacking between 400 and 600°C, it is possible to anticipate that the Zircaloy cladding material undergoes at least two different types of SCC mechanism in the temperature region defined by the "normal reactor operation" and the "accident conditions". A reason for this could be the complexity of the chemistry of the system Zr-iodine, which shows a varied behavior in the cited temperature range /32,33/.

The disappearance of SCC of Zircaloy with increasing temperature (at approx. 850°C), as repeatedly reported in our earlier publications /15,16,17,18/, might be attributable to an insufficient iodine concentration and not to the temperature. In these experiments the iodine concentration varied between 4 and 10 mg/cm^3. However, considering the present state of our knowledge, this iodine concentration is too low so that influences by SCC above 800°C can no longer be expected (Figs.4, 5).

6. CONCLUSIONS

- The out-of-pile experiments with fission product containing Zircaloy-4 tube specimens have revealed that iodine can cause a low ductility failure of the Zircaloy-4 cladding tubes as a result of SCC up to about 800°C. Iodine partly has an effect also in the time-to-failure of the tube specimens. By contrast, CsI does not exert an influence on the mechanical properties of Zircaloy-4. Selenium and tellurium partly produce a reduction in burst strain which, however, is not so marked for tellurium as in the case of iodine.
- The critical iodine concentrations determined out-of-pile which result in SCC failure of Zircaloy are in general clearly higher than the iodine concentrations to be expected from considerations of supply and demand in fuel rods on the cladding tube inner surface. This could be one reason why in the in-pile LOCA experiments so far performed an influence of fission products on burst strain has not yet been observed. Other possible reasons are discussed in the paper.
- If one compares the out-of-pile determined critical iodine concentrations with the iodine supply in a fuel rod, e.g., after a burnup of about 35 000 MWd/t, it can be recognized that an influence of iodine on burst strain can probably be expected to occur only in the temperature range of about 600 to 700°C. Only in this temperature range the iodine supply in the fuel rod is higher than the critical iodine concentration required. However, the decisive factor influencing the impact of iodine is its availability on the cladding tube surface. It depends decisively on the release of iodine during the LWR transients and on the fraction released during pre-irradiation.
- The critical iodine concentration which results in a low ductility failure of Zircaloy-4 tubing at 700°C amounts to about 0.7 mg/cm^3. This iodine concentration corresponds to the fission iodine generated in a LWR fuel rod after a approximately 1.2 at.% ($\approx$ 10 000 MWd/t), assuming total release of iodine from UO_2 in the elemental form. This iodine concentration is within the range of values determined by other ivestigators /33-41/ for normal reactor operation temperatures (300-350°C).
- According to the test results, a change of the mechanism leading to iodine SCC of Zircaloy tubing seems to take place between 600 and 700°C. For this reasons, the critical iodine concentration values determined at high temperatures ($\gtrsim$ 700°C) cannot be extrapolated to lower temperatures ($\lesssim$ 600°C).
- The probability that the volatile fission products can exert an influence on the mechanical properties of Zircaloy-4 in case of ATWS and RIA transients is very high as results from considerations performed in analogy with ramp experiments. Although the discrepancy between iodine demand and iodine supply is similarly great for the ramp experiments, the cladding tube can fail as a result of SCC.
- The safety relevant importance of these out-of-pile test results is due to the statement that the effect of iodine could restrict cladding tube strain to values wich are not critical with respect to the flooding of the reactor core in LOCA transients.

7. ACKNOWLEDGEMENTS

We wish to thank Professor Dr. W. Dienst and Dr. O. Götzmann for their critical suggestions during the preparation of the manuscript. We also gratefully acknowledge the assistance of Mr. H. Metzger in performing the experiments and the metallographic investigations, and Mr. J. Burbach for the SEM investigations.

8. REFERENCES

/1/ P. Hofmann, KfK-2785 (1979)

/2/ W.J. Bailey, C.L. Wilson, L.J. Mac Gowan, P.J. Pankaskie; COO-4066-2, PNL-2488 (1977)

/3/ ANS Topical Meeting on "Water Reactor fuel Performance, St. Charles, Illinois, USA (1977)

/4/ J.C. Wood, Review of Session "Mechanisms for Pellet Cladding Interactions" of the ANS Topical Meeting (ibid), AECL-5850 (1977)

/5/ Meeting on "Ramping and Load Following Behavior of Reactor fuel", Petten, The Netherlands (1978), EUR 6623

/6/ ANS Topical Meeting on "LWR Fuel Performance", Portland, Oregon, USA (1979)

/7/ C. Vitanza; HPR-241, Enlarged Halden Programme Group Meeting, Lillehammer, Norway (1980)

/8/ R. Holzer, D. Knödler, H. Stehle; paper presented at /3/ pp. 207-218, Journ. of Nucl. Mater. Vol.87 (1979) pp. 227-235

/9/ H.S. Rosenbaum; GEAP-23773-2 (1979)

/10/ W.T. Grupp, M.H. Morgan III; paper presented at /3/ pp. 295-304

/11/ H. Zimmermann; paper presented at /7/

/12/ P. Hofmann, C. Politis; Meeting on "Thermal Reactor Safety", Sun Valley, Idaho, USA (1977) CONF-770708, pp. 3-43 / 3-59

/13/ P. Hofmann, C. Politis; Jorn. of Nucl. Mater. Vol.87, Nos. 2+3, (1979) pp. 375-397

/14/ P. Hofmann, C. Politis; 4th International Conference on "Zirconium in the Nuclear Industry", Stratford-upon-Avon, England (1978), ASTM-STP-681, pp. 537-560

/15/ P. Hofmann; ibid. pp. 409-428

/16/ P. Hofmann; Journ. of Nucl. Mater. Vol.87, No.1 (1979) pp. 49-69

/17/ P. Hofmann; KfK-2661 (1978)

/18/ P. Hofmann; European Symposium on "The Interaction between Corrosion and Mechanical Stress at High Temperatures", Petten, The Netherlands (1980)

/19/ H. Lehning, K. Müller, D. Piel, L. Schmidt; Annual Meeting "Kerntechnik 1980", Berlin, Germany (1980), pp. 231-234

/20/ M. Bocek, C. Petersen, L. Schmidt, E. Toscano; paper presented at this meeting

/21/ R.P. Gangloff, L.F. Coffin; Report No. 79CRD016 (1979) to be published in the Journ. of Nucl. Mater.

/22/ P. Hofmann, P. Müller; unpublished results

/23/ W.T. Grubb, M.H. Morgan III; paper presented at /14/, pp. 145-154

/24/ R. Kohli, F. Holub; Nuclear Technology, Vol.48 (1980), pp. 70-76, SGAE Rep. No. A0125 (1980)

/25/ D. Cubiciotti, J.H. Davies; Nucl. Sci. Eng., 60 (1976) p. 314

/26/ M. Peehs et al.; IAEA Specialists' Meeting on "Internal Fuel Rod Chemistry", Erlangen, Germany (1979), to be published in Journ. of Nucl. Mater.

/27/ E.H. Karb; Nuclear Safety, Vol.21, No.1 (1980),pp. 26-37

/28/ L. Sepold; unpublished results

/29/ J.H. Davies, F.T. Frydenbo, M.G. Adamson; Journ. of Nucl. Mater., Vol.80 (1979), pp. 366-370

/30/ F. Sontheimer, W. Vogl. I. Ruyter; Journ. of Nucl. Mater., Vol.88, No.1 (1980), pp. 131-137

/31/ E. Karb, M. Prüßmann. L. Sebold, P. Hofmann, C. Petersen, G. Schanz, H. Zimmermann; KfK.3028 (1980)

/32/ D. Cubiciotti; paper presented at /26/

/33/ M. Peehs et al.; Journ. of Nucl. Mater., Vol.87 (1979), pp. 274-282

/34/ C. Busby et al.; Journ. of Nucl. Mater., Vol.55 (1875), pp. 64-82

/35/ K. Une; Journ. of Nucl. Sci. & Techn., Vol.14, No.6 (1977), pp. 443-451

/36/ K. Une; Journ. of Nucl. Sci. & Techn., Vol.16, No.9 (1979), pp. 660-670

/37/ J.G. Weinberg; Bettis Atomic Power Laboratory Rep., WAPD-TM-1048 (1974)

/38/ A. Garlick and P. Wolfenden; Journ. of Nucl. Mater., Vol.41 (1971), p. 274

/39/ J.C. Wood; Journ. of Nucl, Mater., Vol.45 (1973), p.105

/40/ B. van der Schaaf; ASTM/AIME Symp. on "Zirconium in Nucl. Applications", Portland, Oregon, 1973, STP 551, p. 479

/41/ K.J. Moon, B.H. Lee; Journ. of Korean Nucl. Soc., Vol.10, No.2 (1978), p. 65

/42/ T.R. Yackle, P.E. Mac Donald, J.M. Broughton; paper presented at /7/

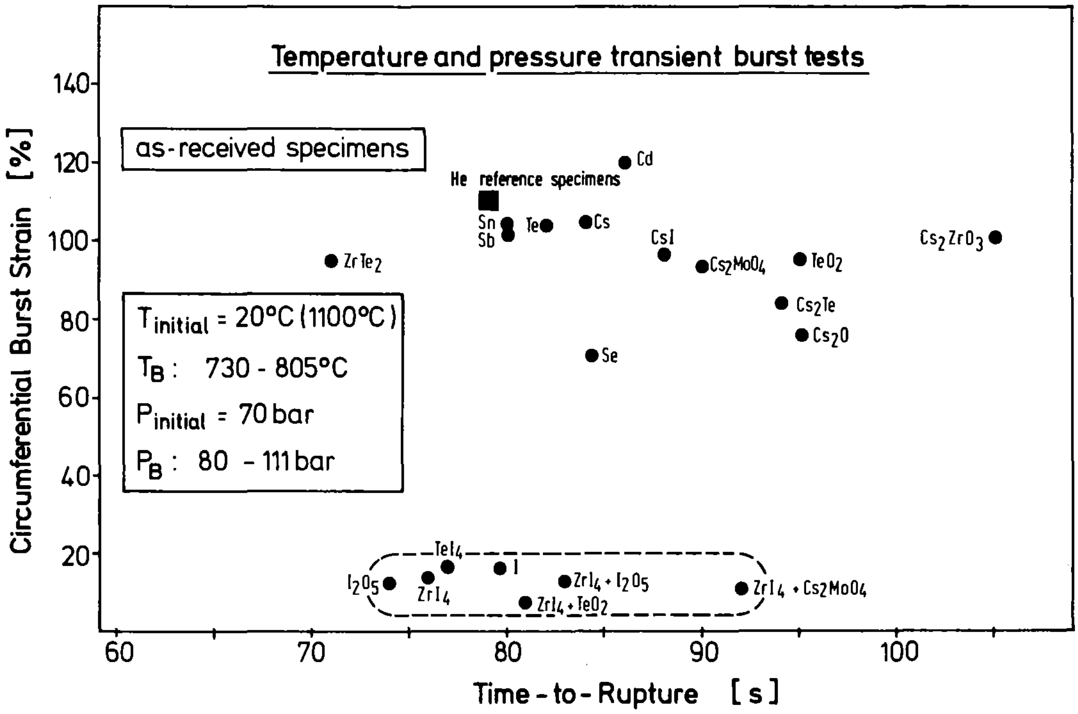

Fig.1: Effect of simulated fission products on the burst strain and time-to-failure of as-received Zircaloy-4 tubing in temperature and pressure transient burst tests in He.

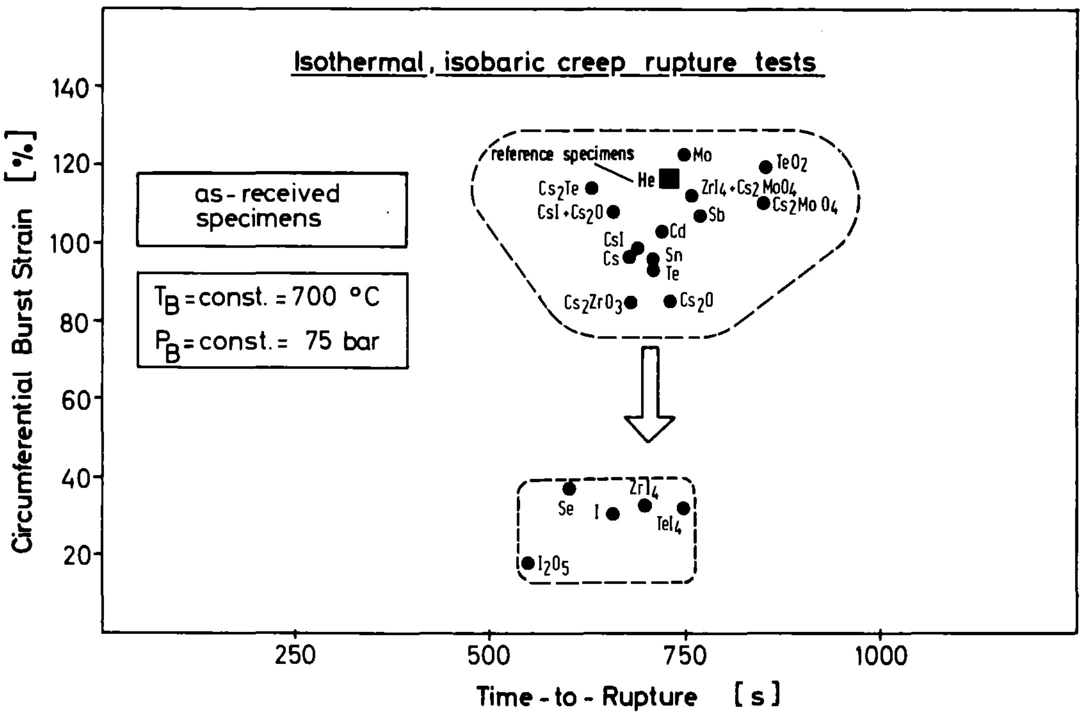

Fig.2: Effect of simulated fission products on the burst strain and time-to-failure of as-received Zircaloy-4 tubing in isobaric creep rupture tests at 700^{o}C in He.

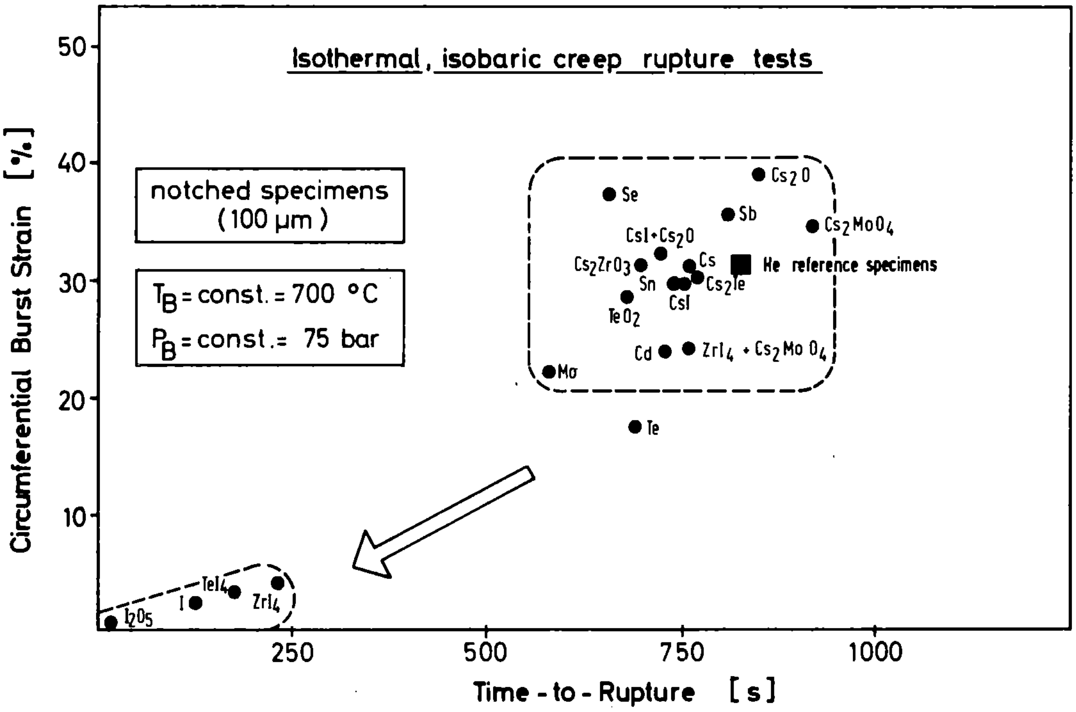

Fig.3: Effect of simulated fission products on the burst strain and time-to-failure of notched Zircaloy-4 tube specimens (100 µm deep internal notches) in isobaric creep rupture tests at 700^{o}C in He.

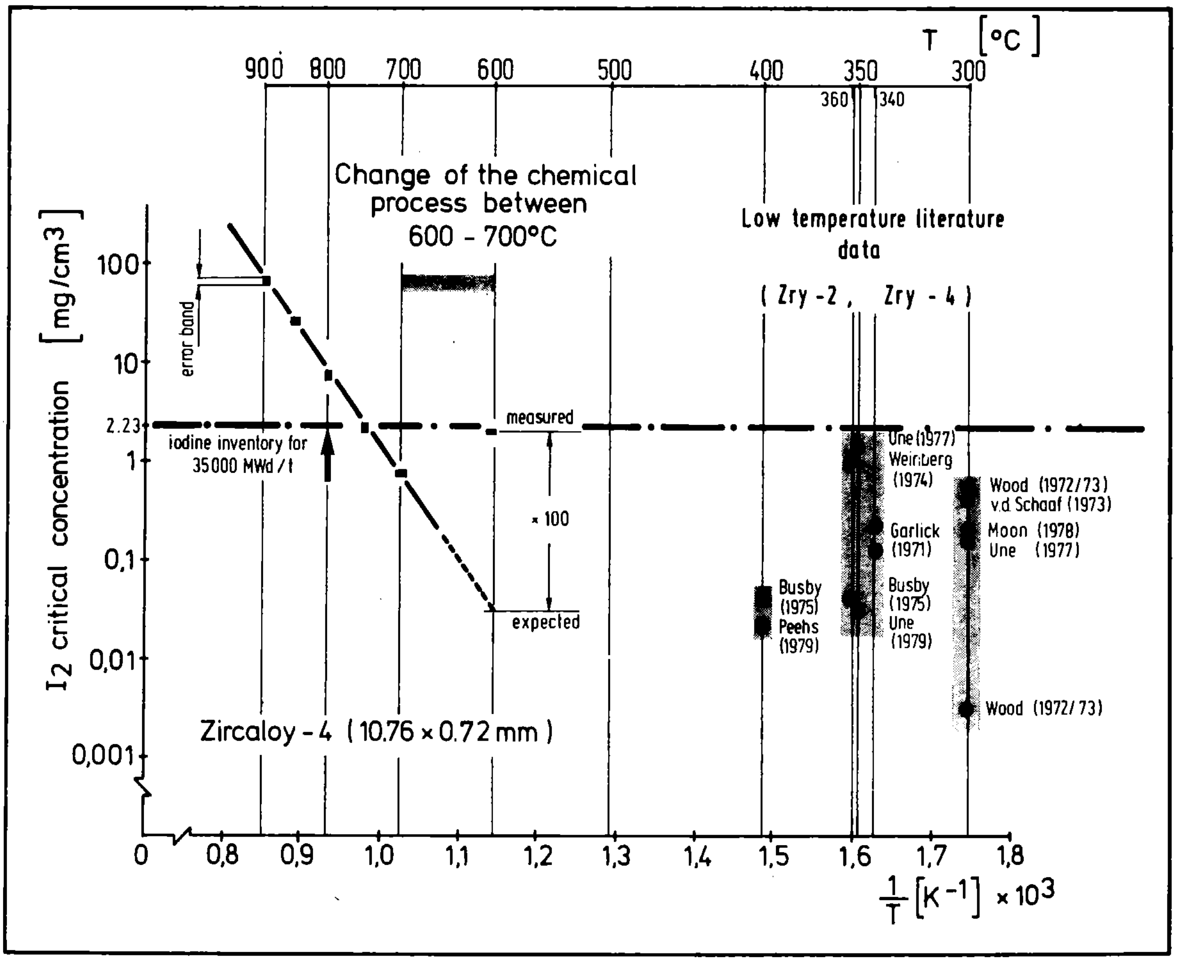

Fig.5: Critical iodine concentration which results in stress corrosion cracking of as-received Zircaloy-4 tubing as a function of temperature.

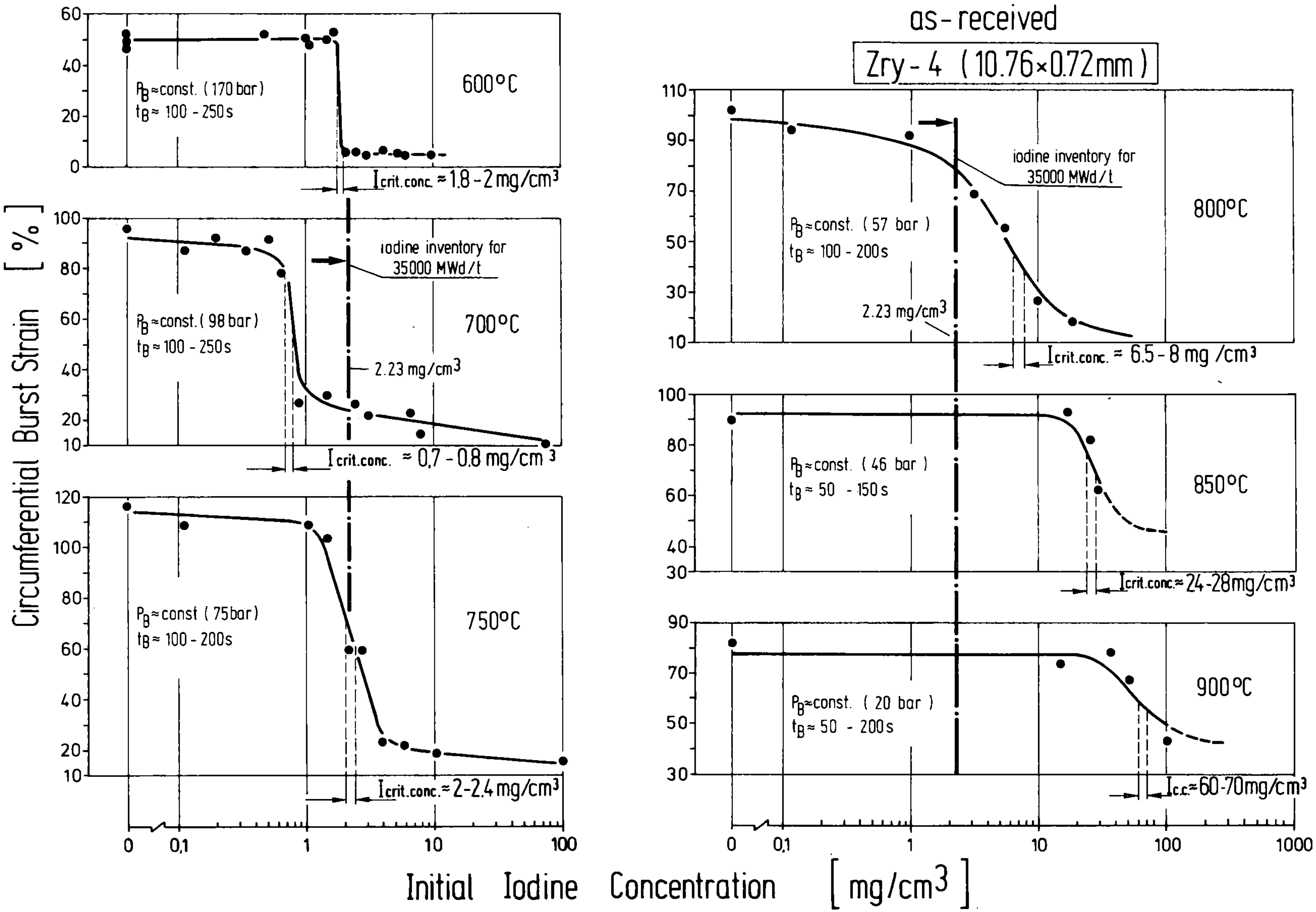

Fig.4: Influence of the initial iodine concentration on the burst strain of as-received Zircaloy-4 tubing between 600 and 900°C in He.

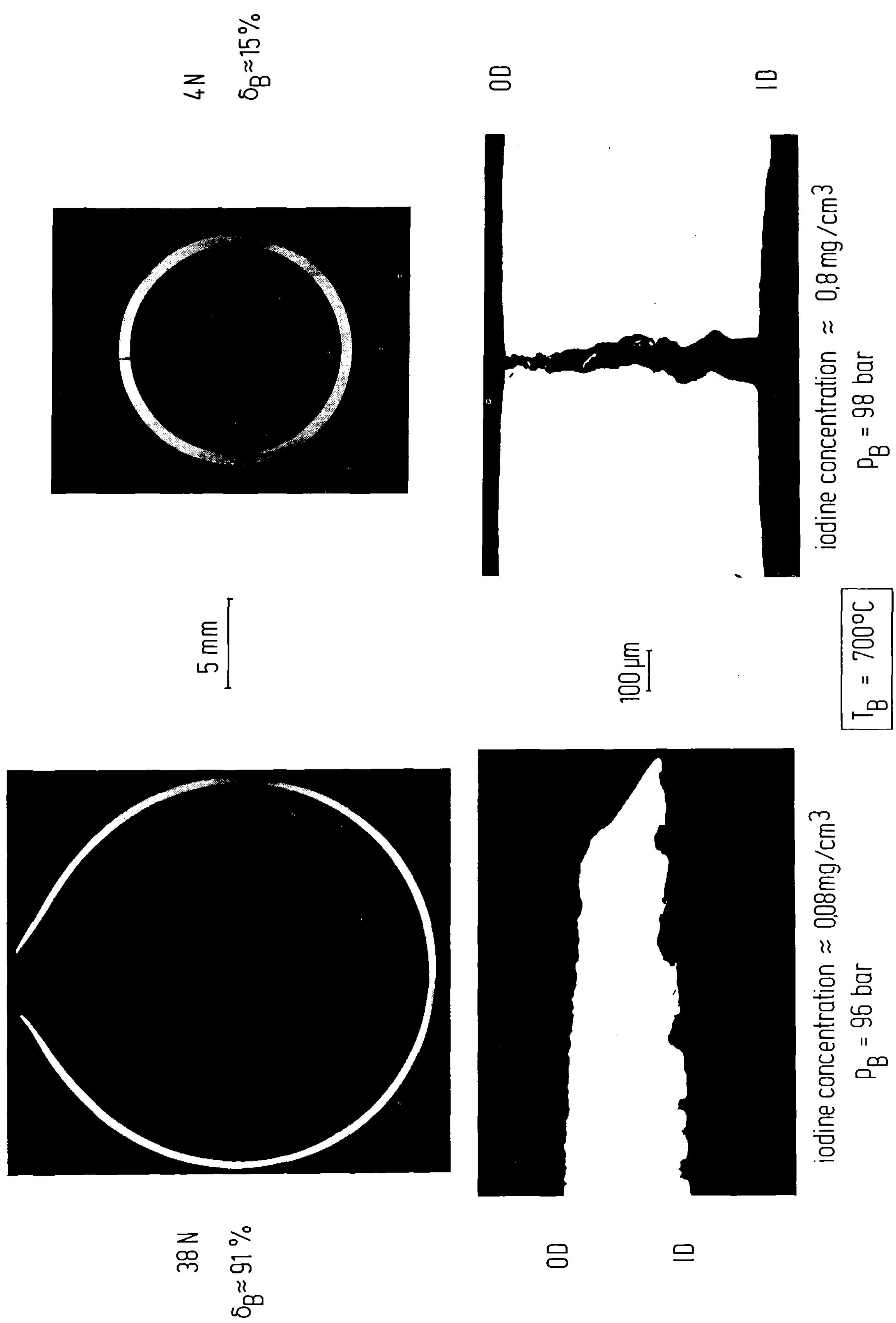

Fig.6: Cross section of as-received Zircaloy-4 tubing after failure under helium-iodine-gas pressurization at 700°C in He. Influence of iodine concentration on burst strain and rupture behavior.

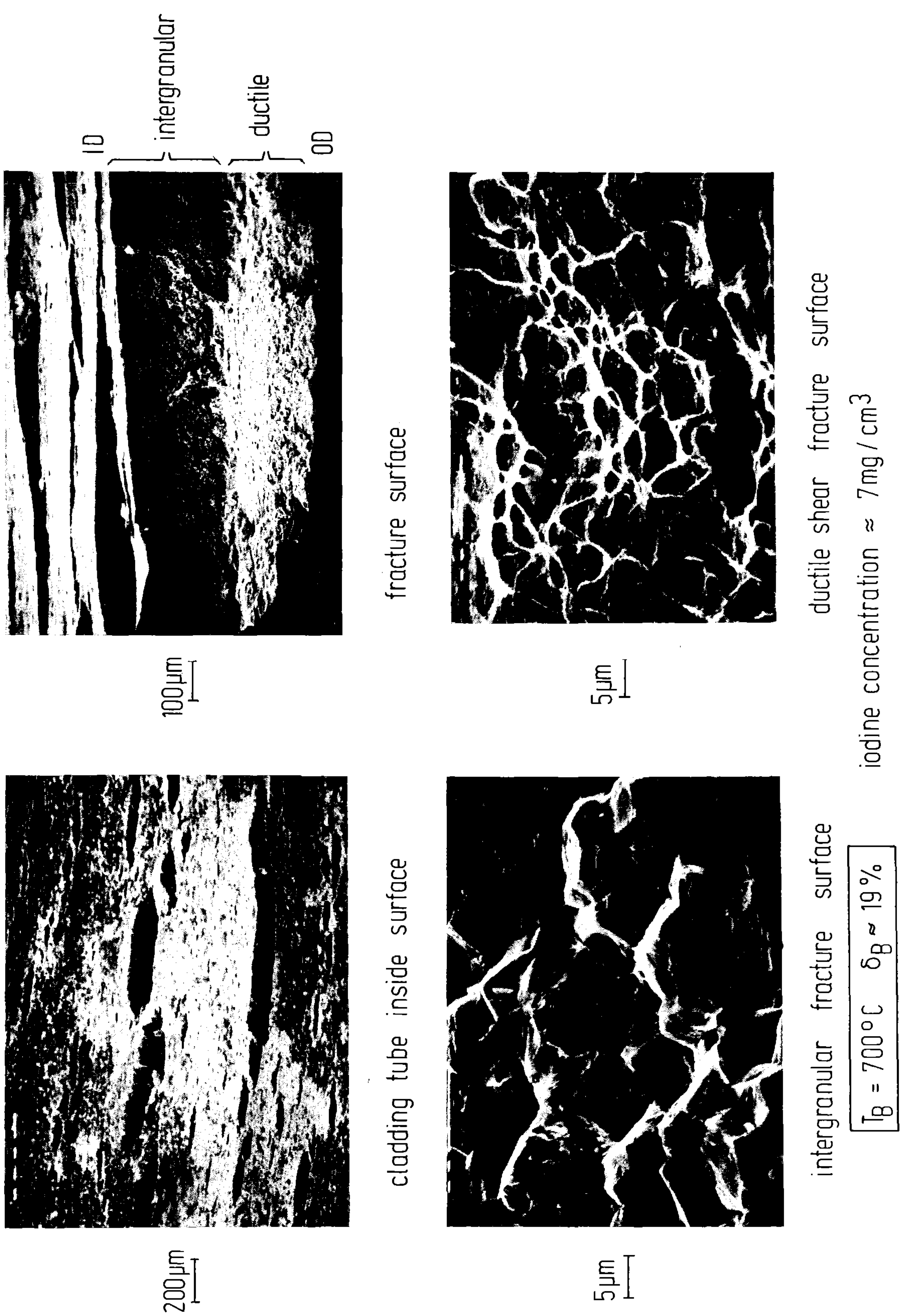

Fig.7: Zircaloy-4 cladding tube inside surface and fracture surface after failure under helium-iodine-gas pressurization at 700°C. The high initial iodine concentration of 7 mg/cm³ leads to a low ductility failure of the Zircaloy tubing. The fracture occurs in a "brittle" mode.

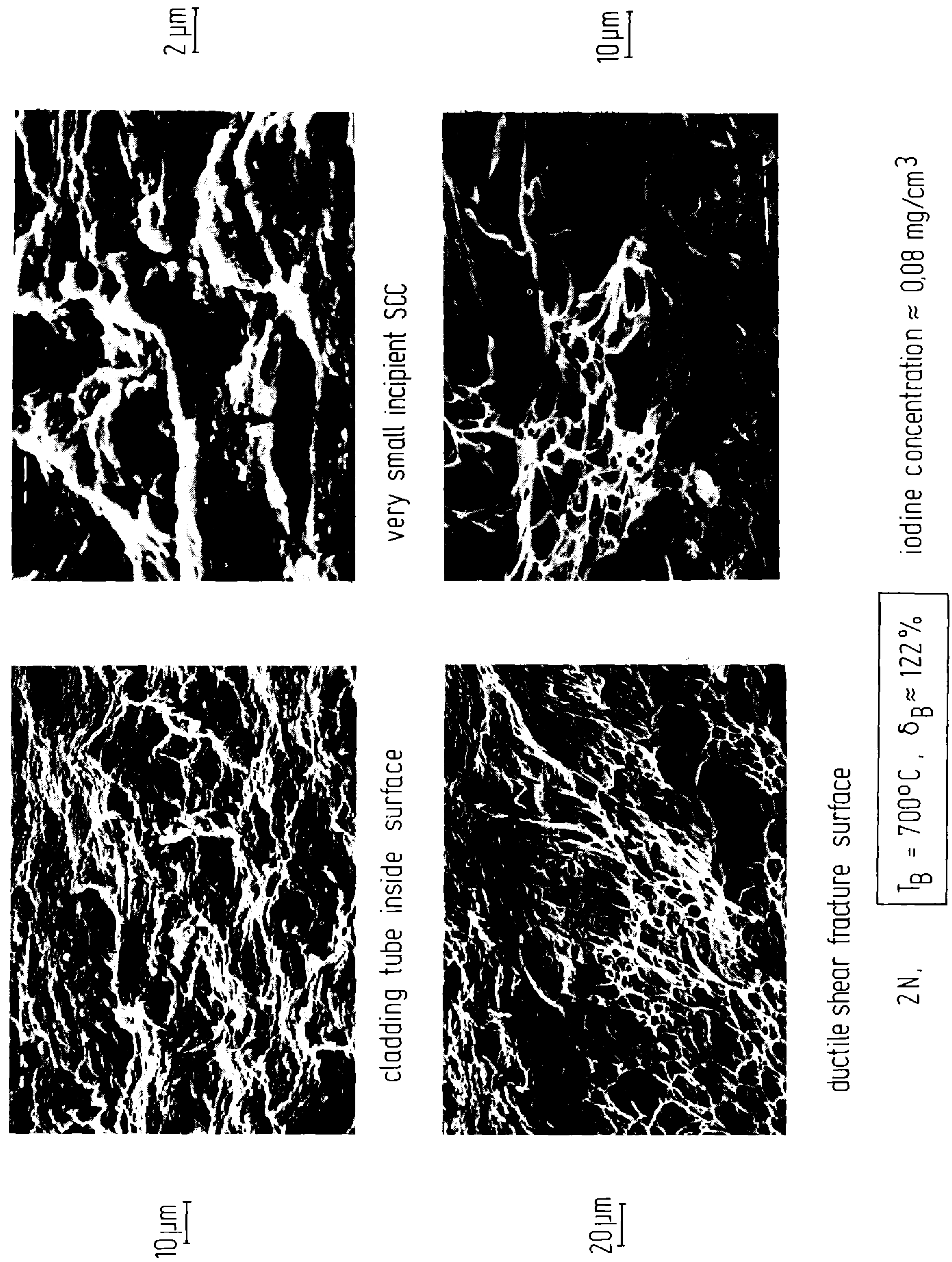

Fig.8: Zircaloy-4 cladding tube inside surface and fracture surface after failure under helium-iodine-gas pressurization at 700°C. The low initial iodine concentration of 0.08 mg/cm^3 has no influence on the fracture behavior. The fracture occurs in a ductile mode.

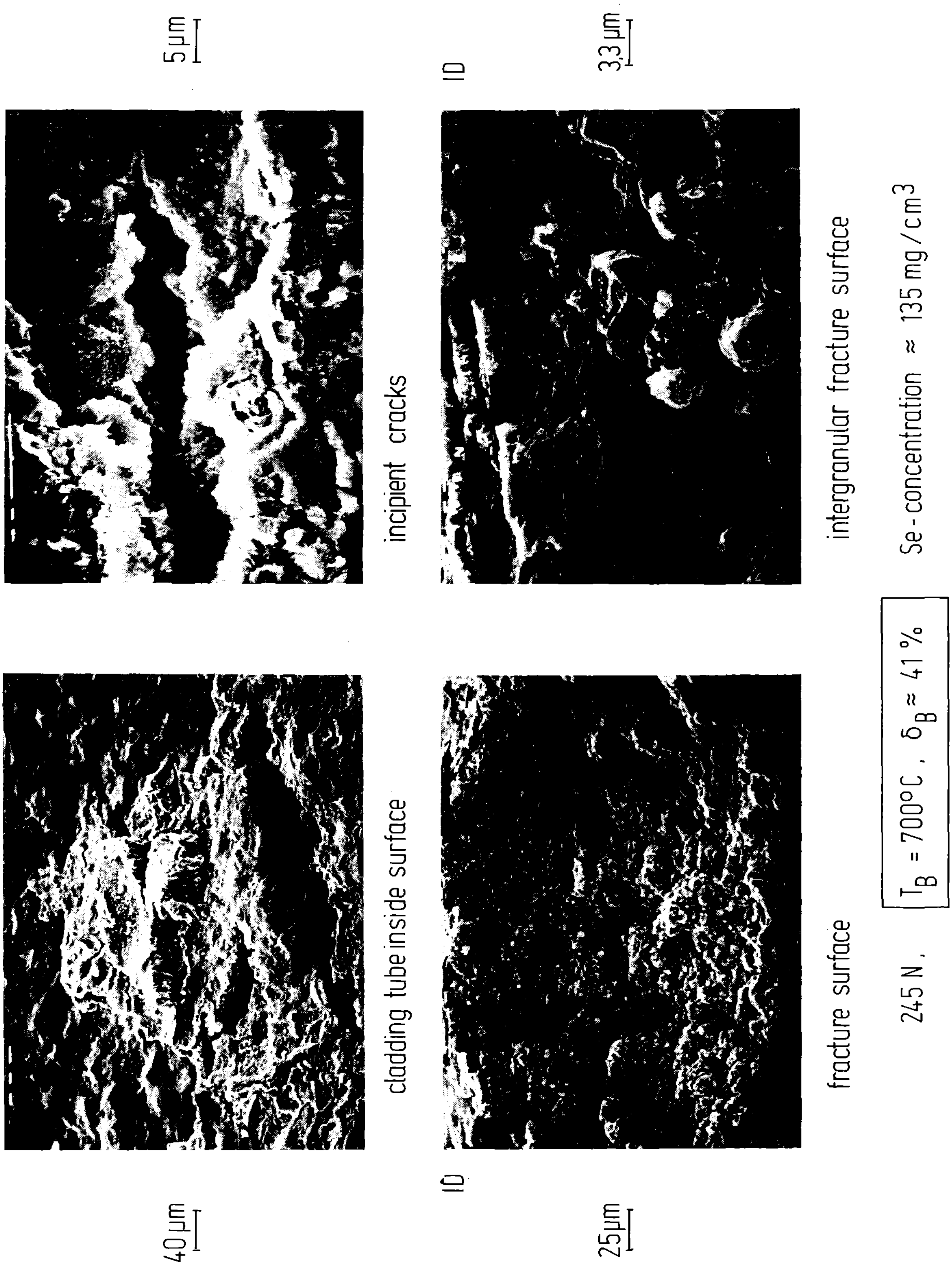

Fig.9: Zircaloy-4 cladding tube inside surface and fracture surface after failure by helium pressurization at 700°C and a selenium filling.