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Recommendations and Supporting Information on the Choice of Zirconium Oxidation Models in Severe Accident Codes

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Abstract

Fuel rod cladding oxidation is one of the key aspects of the accidental behaviour of LWR fuel elements, and a comprehensive base of experimental information on its kinetics is available. However, the conventional treatment of zirconium oxidation kinetics in some severe accident (SA) codes is unsatisfactory compared to the more recently implemented highly sophisticated core degradation models.

Based on a review of experimental results recommendations for application are given in the report, in order to promote the acceptance of a common data base for all SA codes. Convergence towards this goal helps to avoid arbitrary user options and allows the focussing of code-to-code benchmarking comparisons to fields of actual and future concern.

Empfehlungen und unterstützende Information zur Modellierung der Oxidation von Zirkonium in Codes für LWR-Störfälle

Zusammenfassung

Die Oxidation der Brennstabhüllrohre ist einer der wichtigsten Aspekte des Verhaltens von LWR-Brennelementen bei Störfällen, und zu ihrer Kinetik ist eine umfangreiche Basis experimenteller Information verfügbar. Jedoch ist deren konventionelle Berücksichtigung in einigen Codes zur Analyse hypothetischer Störfälle unbefriedigend im Vergleich zu den später eingebrachten anspruchsvollen Modellen für die Behandlung des Brennstabversagens.

Auf der Basis einer Übersicht der experimentellen Ergebnisse wird in dem Bericht mit Empfehlungen zu ihrer Anwendung dafür geworben, für alle entsprechenden Codes eine gemeinsame Datenbasis anzuerkennen. Die Verfolgung dieses Ziels trägt dazu bei, willkürliche Optionen der Anwender zu vermeiden, und ermöglicht eine Konzentration des Vergleichs verschiedener Codes auf Gebiete aktueller und künftiger Interessen.

CONTENT

Page

Appendix
Figs. 1 - 8

1. Status and intentions

1.1 Status

Fuel rod cladding oxidation is one of the key aspects of the accidental behaviour of fuel elements. It is known to support an accidental transient by exothermal heat release, to determine the hydrogen source term, and to be accompanied by development of cladding brittleness and degradation. Its importance grows with time scale and especially temperature range from design-basis accidents to hypothetical severe accident (SA) scenarios.

Since the Seventies world-wide experimental efforts have widened the basis of oxidation kinetic and related knowledge. In SA codes the cladding oxidation is treated by using straightforward (but simplifying) correlations or the mechanistic diffusion system approach. Other, more recently developed, sophisticated models have the potential to account for the progression of fuel rod degradation. However, up to now many SA codes offer as default option oxidation kinetics data, implemented before the whole experimental information was available. Moreover, some code users select oxidation kinetics options according to the best overall fit of their calculation, which might be due to compensating errors. Other users even tend to change options from case to case in the sense of “screw trimming”. Under those circumstances the meanwhile advanced potential of the codes is not accessible and the benefit from mechanistic models not granted. Discrepant data bases complicate code-to-code comparisons unnecessarily.

Instead, it is recommended to re-consider the body of available experimental information on zirconium oxidation kinetics, to select the most reliable data and to apply them as common data base for all SA codes. Erecting every different code construction on the same sound oxidation kinetics fundament will help to avoid unnecessary and arbitrary code user decisions and will allow to focus benchmarking comparisons to fields of actual and future concern.

1.2 Actions within COLOSS

In the Minutes of the COLOSS Kick-off Meeting [1] the objectives of the project are summarised by the sentence: “The COLOSS project aims at reducing some uncertainties related to reactor core degradation under Severe Accident (SA) conditions.” The objective of Work Package 8 on plant applications is “to assess the ability of SA codes to calculate severe degradation phenomena in adequate details and with sufficient accuracy and to evaluate the impact of new models on the H_2 release, on corium formation / progression and on the source term”.

During the 3rd Progress Meeting, the Mid Term Assessment (MTA) Meeting of the project, discussions arose on the impacts of the choice of different correlations for the treatment of fuel rod cladding oxidation in plant calculations with different code systems [2]. It was argued that any reasonable agreed choice would be advantageous for benchmarking purposes, and that the best adequate choice would improve the accuracy of SA calculations. On this basis the effects of implemented new models should become better obvious.

At the 4th Progress Meeting a draft text version was presented, together with illustrations, available from earlier studies of the department of Leistikow and co-workers at KfK (now FZK), to which the author was contributing. At the 5th Progress Meeting it was decided for practical reasons to apply proposed interim recommendations for sensitivity studies within the 2nd set of plant analysis group (PAG) calculations to be performed and analysed in a final COLOSS document.

Agreement was reached that further improved treatment of oxidation kinetics in SA codes beyond the COLOSS time scale is an important task, in which other relevant items as steam supply limitation, cladding wall consumption and clad failure criteria have to be considered as well.

2. Historical background of experimental data

2.1 Judgement of historical strategies

In the Seventies the risk of "fuel rod shattering" due to cladding embrittlement by steam oxidation in accidental reactor situations became an important issue. The report of Scatena [3] illustrates the knowledge and strategy of that time. In USA the so-called Interim Acceptance Criteria demanded mandatory in 1971 to restrict the extent of the Zr/steam reaction with respect to hydrogen release and set the limit of the peak temperature at 1533 K (1260 °C, 2300 °F) with respect to retained coolable geometry. Novel Acceptance Criteria, defined in 1973, prescribed a temperature limit of 1477 K (1204 °C, 2200 °F), long-term coolability, a global hydrogen release limit corresponding to 1% consumption of fuel-bearing cladding, and a calculated limit of 17% local cladding conversion to ZrO_2. The calculation procedure for the latter percentage was understood to use the oxidation correlation of Baker and Just [4] and to refer to the circumferential wall thickness average of the ballooned or burst cladding at onset of considerable oxidation. Since then similar acceptance criteria were prescribed by safety authorities in many other countries. The Baker-Just correlation itself is based on results of their own experiments for just the melting temperature of zirconium, (in which fine Zr wires were directly heated in water and the hydrogen evolution from the resulting molten droplets was measured to calculate the reaction rate), together with literature results from Lemmon and Bostrom, who used inductive specimen heating and a hydrogen evolution measurement for evaluation (citation e.g. in [13]). The Baker-Just correlation is to be seen as most important in the described historic context and well justified up to now for licensing purposes. As conservative approach it should not be considered for best estimate calculations.

Presently, there is a revision of the acceptance criteria in order to take into account the use of higher fuel burn-up in power plants and new cladding Zr-Nb alloys. This revision could induce additional oxidation studies.

The philosophy of using conservative limitations changed into the effort to identify best estimate descriptions of the real materials behaviour. In this sense the evaluation of "embrittlement" studies at Argonne National Laboratory correlated the residual ductility of oxidising cladding with the layered compound microstructure of Zr matrix, oxygen-stabilised α-Zr and ZrO_2 scale, and the oxygen profile in this diffusion couple [5]. This effort and others of this kind (e.g. by Sawatzky, see [19]) profited from a wealth of published information from oxidation kinetics studies performed simultaneously since the early Seventies in various countries.

Before continuing in systematic and detailed reporting, a few selected illustrations on this new requirement to consider the real instead of the "worst case" materials behaviour are introduced. The scheme of the diffusion system Zircaloy / steam, Fig. 1, is taken from a publication by Chung at ANL, which initiated much controversial response, related to the terms "steam starvation" and "hydrogen blanketing" (reference given in the figure). The phase diagram information, available at that time, was combined at KfK [9] to the Zr-O system of Fig. 2, which is often used up to now. Fig. 3, composed at KfK, is a complex synthesis of the new embrittlement criteria proposal by the ANL team [5] (right side) and the kind of information, required for application (left side): An overlay graph consists of the oxygen concentration profile across the wall of a double-sided oxidised Zry tube specimen according to calculation with SIMTRAN [8], together with a cross section of a specimen from the KfK test program, showing good representation of the layers growth kinetics by the verified code.

2.2 Experimental results on oxidation kinetics of zirconium alloys

In the present context it is not necessary to give a comprehensive description of all efforts, which differed in experimental and evaluation procedures, scope and, consequently, precision. Instead, the more recent and the actually considered studies are stressed.

Starting with a most ambitious effort the Zirconium Metal-Water Oxidation Kinetics Program (ZWOK) of Oak Ridge National Laboratory (ORNL) is summarised: Isothermal oxidation experiments on Zircaloy-4 tube specimens in flowing steam and in two furnace-heated facilities covered 1173 to 1773 K in 50 K steps. The kinetic evaluation of metallographic measurement of ZrO_2 and α-Zr(O) layer thicknesses was accompanied by calculated approximation of oxygen uptake in comparison with some weight gain measurements. Deviations from parabolic behaviour below 1273 K were the reason for excluding results for lower temperature from the formulated Arrhenius type correlations, which were given for the rate coefficients of the growth of scale, α-Zr(O) layer, the combined double layer and the oxygen uptake. (For application it is of course important to notice that the rate equations, given in the final report on kinetics [6], correspond to the integrated form of the parabolic rate law, as indicated by their form of denomination as $\delta^2/2$). Temperature transient experiments have proved general consistence with isothermal kinetic results, whereas some anomalies were related with the hysteresis of the phase transformation between tetragonal and monoclinic oxide. Information on the limited influence of high steam pressure is covered in another final report. In the ORNL ZWOK program the strong temperature dependence was considered by most careful temperature measurement and TC calibration. The transient heating of the specimens was taken into account by corrective reduction of the exposure to ideal isothermal conditions.

In an accompanying study the oxidation was modelled by Pawel [7] in terms of diffusion coefficients of the layered compound, and after solution of the problem the model was verified in comparison with the experimental results by deducing the diffusivities of the oxide and the α-Zr(O) phase. Insufficient sensitivity for an evaluation of the diffusivities in β-Zr was the reason for a measurement program in the 900 to 1500 °C range with different methods and evaluation procedures, as documented in another final report. On the basis of those studies Malang, visiting scientist from KfK, developed the mechanistic code SIMTRAN dedicated to the treatment of materials oxidation during accidental transients [8], see Fig. 4.

The experimental program on Zircaloy-4/steam oxidation kinetics and related behaviour performed by Leistikow et al. at FZK (the former KfK), initiated in 1973, developed during the years into a comprehensive effort. The first program covered isothermal oxidation kinetics experiments in the range 1173 to 1573 K, in steps of 100 K, performed with short tube sections, exposed to flowing steam in tubular furnaces. The kinetic evaluation covered all tests with respect to the gravimetrically measured weight gain, due to the very limited hydrogen uptake of the specimens corresponding to the oxygen uptake. A representative fraction of the specimens were microstructurally examined and evaluated with respect to the kinetics of ZrO_2 scale, α-Zr(O) phase and double layer of both [9]. The nomenclature used for the parabolic reaction rate coefficients indicates that the ZWOK program served for orientation. In contrast to the ORNL correlations validity was claimed here for the temperature range 973 to 1573 K covered meanwhile, despite considerable deviations from ideally parabolic kinetics on the longer durations below 1273 K. Mainly this decision is the reason for some discrepancies between the correlations from FZK and ORNL. Whereas the evaluation procedures were less standardised and had to rely more on “engineering judgement” compared to ORNL, the advantage of the data base is its size (some hundred isothermal tests, more than 1000 in total for all studies) and the availability of experimental oxygen uptake results for all kinetics experiments. Scoping tests with Zircaloy 2 showed no significant influence of alloy composition. The fair agreement with the ORNL results despite all differences in procedures was surprising and convincing. In a systematic study transient experiments in form of idealised LOCA type were performed by inductive specimen heating.

Moreover, other groups have published rather similar kinetic results from programs performed at that time, all using furnace heating. Kawasaki et al. from JAERI [10] and Brown and Healey from UKAEA [11] shall be cited. An early comparison of the results of different experimental groups was performed with statistical methods [12].

The often considered correlations of Urbanic and Heidrick refer to different experimental and evaluation procedures [13]: Inductive heating of the rod-shaped specimen took place submerged in a water-filled Vycor glass column in one test series. Temperature control via Pt-Pt10Rh thermocouple in a closed alumina support tube was combined with pyrometer monitoring. Reaction kinetics and the rate of growth of the combined ZrO_2+α-Zr(O) layer for Zircaloy-2 and Zircaloy-4 in steam were measured over the temperature range 1323 – 2123 K. Continuously registered hydrogen evolution was used for evaluation of oxygen uptake and metallographic procedures for layers thickness measurement. In another test series the specimen was inductively heated and exposed to flowing superheated steam, in order to demonstrate that hydrogen evolution had no limiting influence on steam supply in the first test procedure. The deviation of the results to those of the before referred authors, especially concerning the temperature trend, gives rise to objections: Due to the fact that it is difficult to avoid inhomogeneous specimen heating by an inductive method, some doubt is justified if Urbanic and Heidrick have always deduced meaningful specimen temperatures. The authors were the first to identify a discontinuity in the Arrhenius plots of the rate coefficients for mass increase, ZrO_2 layer and the combined ZrO_2+α-Zr(O) layer, but not for that of the growth of the α-Zr(O) layer alone. Those results were discussed in relation with the formation of the cubic ZrO_2 modification. For its lower stability limit 1853 K was given according to the phase diagram.

A program at Worcester Polytechnic Institute by Biederman et al. [14] used direct resistance specimen heating within an (unheated) reaction chamber, purged by superheated steam. The facility allowed external and/or internal tube oxidation. Objections against this procedure relate to temperature homogeneity and gas flow. The program was continued to study the influence of pre-oxidation, (unfortunately not reasonably evaluated), and deformation under internal overpressure.

Both groups found considerably lower activation energies for the Arrhenius representations of their results compared to those of the groups covered in the previous sections. Ocken [15] surveyed and discussed the results available at that time in favour of the before mentioned EPRI funded programs [13,14]: He stated that their advantage would be the temperature gradient from heated specimen to cool surrounding, leading to temperature gradients in the cladding wall in the same sense as in a reactor. In total disagreement with the argument of Ocken the author of this paper stresses the advantage of a constant cladding wall temperature and thus of a better defined specimen temperature, as provided in furnace experiments! This point is instead the reason for serious doubts in the reliability of the test temperature interpretation for both programs [13,14] which used inductive (Urbanic and Heidrick) or direct electrical heating (Biederman et al.) of a specimen in a cool environment. This argument was already used by Sawatzky et al., who performed similar studies with inductive specimen heating as Urbanic and Heidrick. Sawatzky reached an important improvement of the specimen temperature homogeneity by only optimising the geometry of the specimen and registered considerably increased reaction rates. This result clearly supports the furnace test preference in contrast to OCKEN´s argument.

It is therefore recommended not to consider the Urbanic-Heidrick correlations for application in SA codes. Their low-temperature correlation over-estimates the oxidation towards lower temperature. Their high-temperature branch under-estimates oxidation with increasing temperature.

After this most productive period some activities continued towards the higher temperatures considered to be reached in hypothetical severe accidents and with respect to related topics. At FZK the kinetic studies were expanded towards higher temperatures, longer exposure (breakaway effect), the interrelation between cladding oxidation, deformation and bursting, and finally steam starvation and hydrogen reaction. With respect to the first item new furnace experiments were performed in the 1573 to 1873 K range in 50 K steps by Aly [16] and re-evaluated (by the author of this report) according to the established procedures (Fig. 5). So consistent results for the full temperature range 873 to 1873 K could be presented [17]. The earlier published correlations proved to be applicable unchanged up to 1773 K. Microstructures for 1823 and 1873 K clearly showed cubic ZrO_2 phase as internal part of the double-layered oxide scale and enhanced kinetics, explained by the broader sub-stoichiometry and higher oxygen diffusivity of that phase (Fig. 6). According to our results cubic ZrO_2 and related kinetic change should be taken into account from ~1525 °C (1800 K), which is slightly below the figure given by Urbanic and Heidrick (1853 K). However, the co-existence of cubic and tetragonal phase in a broad temperature range above clearly excludes the use of a step function, as proposed by them, but demands, instead, a smoothing of the step in order to get a steady transition from the high-temperature to the low-temperature correlation. To be clear, this proposal means that the HT and LT correlations ought to be combined within the temperature range of duplex scale by use of adequate (temperature-dependent) weighting factors. Those would have to represent the oxygen flux match through the duplex scale, and would depend on the sub-stoichiometry ranges and the diffusivities of both sub-layer phases. This would give a curvature of the HT branch in the Arrhenius plot of inverted S-shape downward towards the LT branch, reached at 1800 K. The described difficulties indicate practical limits of development potential for the simplified correlations approach.

In contrast, such a refined treatment can be performed better, since without any arbitrary assumptions, with a mechanistic code, in which the diffusion profile is calculated on the basis of diffusivities and phase boundary concentrations. Of course, uncertainties in the phase relations have to be resolved for that purpose.

Fortunately, the HT region was covered with new experiments of adequately fast control procedure: Prater and Courtright performed experiments in steam by heating one side of the disk specimen by a defocused CO_2 laser beam for varying time and measuring temperature at one or the other side by a two-colour pyrometer [18]. Computer coupling of pyrometer output and laser power control permitted rapid and reproducible temperature control to pre-programmed time sequences. This procedure resulted in strong, unavoidable temperature gradients across the specimen, so that caution is indicated, similar to the arguments against the Urbanic-Heidrick data. By evaluating the layer thickness growth for front and back side and averaging the authors could, however, provide rather convincing kinetic data for ZrO_2 layer growth, ZrO_2 plus α-Zr(O) double layer growth and oxygen consumption, approximated thereof (Fig. 7). Satisfactory comparison with the two temperature points 1823 and 1873 K provided in the work at FZK can be registered. Due to the known experimental difficulties the base of HT data remains small and possibly not fully exact up to now.

This argument can be used to lead over to other still unresolved sources of uncertainty in the calculation of the extent of cladding/steam oxidation. The first point refers to gas phase transport controlled oxidation of fresh metallic surfaces. Codes ought to use adequate rate limits for this initial oxidation phase. Another point is related with internal steam oxidation after cladding perforation or fracture, which will occur in a certain range of temperatures. This behaviour is treated by user-defined choice of the burst criteria (LOCA case) and the rod failure criteria of the SA code. The supply of penetrated steam will be consumed in a certain range (~10 cm) around the position of penetration. The local effects close to clad failure can be neglected for integral SA plant calculations. At contact to the fuel, the cladding interior will have already picked up oxygen by diffusion and formed an α-Zr(O) layer before steam ingress is expected. Mechanistic modelling of external steam oxidation parallel to internal fuel interaction has been demonstrated (PECLOX, see below), but inclusion of steam ingress would be an ambitious task.

Cladding matrix melting tends to reduce the surface available for oxidation during rod-internal agglomeration and increases it by the subsequent external dispersion, so that important uncertainties in defining surface areas of reactive molten material will remain. Melt oxidation kinetics differ from that of solid material, a field recently covered, as reported below.

The adequate choice of the correlation for the high-temperature range and its application in SA codes are required with first priority. The above mentioned aspects contribute to remaining uncertainties of calculations and require adjustments and model improvements. The conclusion of the author is that the experimental data base on oxidation kinetics is fairly well defined in comparison to the effect of other sources of uncertainty, which increases with temperature and the degree of damage.

2.3 Kinetics and modelling of temperature-transient conditions

Oxygen transport limitation within the gas phase is considered as one of the rate controlling factors for the oxidation of virgin metallic surfaces during an initial period. More important for the growth kinetics of thick scales are possible regimes of gas phase mass transfer control in cases of extremely high temperature or insufficient steam supply. In all other cases the reaction rates and layers growth are determined by the transport of oxygen within the solid state diffusion system, which is transformed to a multi-layered compound. The only adequate approach for the treatment of temperature transient conditions is to solve the coupled diffusion problem (for the solid compound or even including the gas phase). Knowledge of diffusivities and phase boundary concentrations in temperature dependence is required. Diffusivities can be deduced from oxidation experiments and equilibrium concentrations from the phase diagram. Reliable experimental data and consistent evaluation, not always provided in the past, are most important. Corresponding approaches by Pawel [7] and Malang [8] were already mentioned, more recent ones are covered later.

In contrast, the simple mathematical procedure of integrating experimentally determined isothermal oxidation correlations, as first performed by the WPI team with ZORO 1 [14] has serious drawbacks. Since it relies on the extrapolation of the correlations in time, and does not take care of the limited size and of changes in the relative thicknesses of the layers of the diffusion system, it requires criteria to stop the calculation after β-Zr matrix or α-Zr(O) metal consumption. This straightforward procedure can provide quite fair results for one condition, but is suspect for quite poor description of others, especially if fast transients are involved. Such approximate correlation approaches are used in SA code systems of integral type. It is important to notice that they are not applicable to situations in which steam supply limitation interferes or even dominates.

In general, temperature-transient experiments have been reported to reflect the kinetics deduced from isothermal ones; however, complications have been mentioned as well. In response to the verification of SIMTRAN 1 against results of transient KfK experiments Malang introduced time constants for the change of boundary concentrations towards the equilibrium values for application in calculations of fast transients, during which those might not be kept. Sawatzky et al. [19] described in detail the temporary formation of duplex sub-layers during cool-down, as well as fast heating, phenomena explained by the temperature dependence of the phase boundary concentrations. Calculations with SIMTRAN, (later on developed into the version MULTRAN in order to account for more layers,) showed that the regular oxygen diffusion profile is disturbed during fast transients. Microstructural results from FZK indicated deviations from SIMTRAN calculations, however, only in the phase of fast cool-down: In addition to the (long-range) oxygen transfer mechanism alone, represented in the code by enhanced α-Zr(O) layer growth due to oxygen super-saturation of the β-Zr matrix, a competing short-range oxygen re-distribution, the precipitation of α-Zr(O) within the super-saturated β-phase matrix, takes place.

Neitzel developed the numerical code PECLOX (<u>pe</u>llet <u>cl</u>adding <u>ox</u>idation), which did not include a coupled temperature calculation as in SIMTRAN, but covered internal cladding oxidation via diffusive oxygen transfer from the fuel pellet. In cooperation with Hofmann the code was verified on the basis of the experimental results of Hofmann et al. on fuel/cladding chemical interaction kinetics [20]. It was demonstrated that, in addition to the formation of external scale, the α/β interfaces of the layered system advanced with comparable kinetics from both cladding surfaces, thus describing the interaction not only until matrix consumption but up to complete conversion of the cladding. It is mentioned that the dissolution of pre-existent scale in inert atmosphere due to oxygen equilibration has been calculated as well. Since such a condition corresponds to the limiting case of “steam starvation”, it is mentioned here that PECLOX has been used (I. Cambien, during her delegation to FZK) to verify dramatic differences in the oxygen concentration profile in case of effective limitation of external steam supply. Code modules, based only on parabolic correlations would fail in treating such conditions.

After development of the deterministic code SVECHA by Veshchunov et al. at IBRAE, Moscow, verification of the oxidation module required the knowledge of reliable diffusion data. The procedures consisted of a thorough analysis of available oxidation kinetics results with respect to their reliability, statistical methods of evaluating the data sets, and the formulation and solution of the coupled diffusion problem [21]. Best-estimate diffusion coefficients for ZrO_2, α-Zr(O) and β-Zr were deduced for the temperature range 1273 to 1773 K and the diffusion coefficient of cubic ZrO_2 for the temperature range 1798 to 2098 K. The thus determined best-estimate diffusion coefficients were successfully validated in [22] against temperature transient tests [17] and [20].

It is further mentioned that the known hysteresis of the tetragonal/monoclinic ZrO_2 phase transformation during temperature cycles gives rise to anomalies in the transient oxidation kinetics in the ~1073 to ~1373 K range, as reported by several authors. (Co-existence of both phases in a temperature range and mutual transformation by a martensitic process of lattice distortion are influenced by the higher density, broader range of sub-stoichiometry and smaller surface energy of the tetragonal phase, compared to the monoclinic one. Consequently, this phase is interpreted to get stabilised towards lower temperatures by compressive stress, sub-stoichiometric composition and small grain size. Those conditions are holding originally and relaxing during continued oxidation.) According to the common opinion high steam pressure tends to stabilise the tetragonal ZrO_2 modification and thus influences the oxidation kinetics, however, only indirectly.

Usually, pre-existent scales are assumed to have and to retain protection properties independent of their formation temperature, thus neglecting potential influences of temperature-dependent scale growth morphology and cracking effects. This idealised view has not been confirmed in own experimental studies, in which the loss of protection of pre-existent scales was registered to set in locally and to proceed during subsequent heating in the range 1300 to 1500 K. Fortunately, the relative influence of the mentioned complications, which are observed at comparatively low temperatures, is rather limited. It is therefore not required to consider them for SA calculations of scale growth kinetics in the present context.

2.4 Summarising statements

- The Baker-Just correlation [4] will retain its importance for comparison and licensing purposes (conservative approach). However, it should not be considered for application in best-estimate calculations. At high temperature, near the melting point of Zry, the correlation is less conservative.
- The Urbanic-Heidrick correlations [13] are based on pioneers´ work of continuing interest. However, serious doubts in both, the given specimen temperatures and their homogeneity (radial and axial temperature gradients), related to the method of inductive heating, are fostered by strong discrepancies in comparison to data gained in test programs using furnace-heating. It is therefore recommended not to consider the correlations for best estimate applications, even if the radial temperature gradient in the experiments should have been similar to the reactor accident case.
- The Cathcart-Pawel correlations [6] and the Leistikow correlations [17] are judged to be of equal and high reliability. This standard is understood to result from strong efforts towards precise temperature measurement and control, the volume of the data bases and adequate and consistent evaluation procedures. Similar results from other programs confirm this judgement. An argument for using a combination of both, in order to reduce sys-

tematic errors of the two sets of measurements, is the recent conclusion of the IBRAE team [21] that both data sets are statistically not different from the combined set.

- Arguments for support of a choice between both sets of correlations are on the one hand the more standardised procedures and the special temperature calibration efforts in favour of the Cathcart-Pawel correlations, and on the other hand the larger data base, the availability of experimentally determined mass gain (oxygen uptake) for all tests and the better fit for lower temperatures in favour of the Leistikow correlations.
- In the temperature range above 1800 K the Prater-Courtright correlations [18] are the unrivalled only choice. Their precision is judged to be considerably inferior due to experimental procedures and evaluation methods, necessary for measuring fast reactions. Observations concerning the scale microstructure in relation to phase stability support the recommendation to smoothen the artificial step at 1800 K between the Cathcart-Pawel / Leistikow correlation and the Prater-Courtright correlation by using a weighted average of both in a range of temperatures between 1800 and ~2600 K, the limits of stability of the duplex scale. Replacement of this procedure would be indicated as soon as more reliable kinetic and phase diagram data should become available.
- Benchmarking against calculations on the basis of diffusion data and interface concentrations is important for justifying the use of correlations and especially with respect to the preliminary procedures of describing the oxidation at highest temperatures, which will be proposed below.

3. Interim recommendations and proposed technical procedures

During COLOSS meetings agreement was reached on the importance of improving the analytical treatment of the fuel rod cladding / steam oxidation in SA codes. This was argued to be a task which cannot be solved by all partners within the COLOSS time scale. The analytical procedures must be physically sound enough to provide the necessary predictive power, and mathematically elegant and simple enough for the incorporation into codes, as well. For actual demands it was found necessary to define interim procedures, requested for the 2nd set of calculations to be performed by the PAG members of COLOSS. It was decided to perform, on voluntary basis and in addition to the main set of calculations, sensitivity studies, in which the influence of the recommended changes is considered.

It is mentioned again that a treatment of the oxidation on the basis of parabolic kinetic correlations instead of solving the diffusion problem for the system remains a compromise, in which the oxidative consumption of the tube wall and the steam supply limitation cannot be considered at all or only by additional simplifying procedures. Despite this it was decided to use the correlations approach as and if foreseen in the respective code.

3.1 Interim recommendations

- In the low-temperature range up to 1800 K the Leistikow correlations ([9], confirmed for extended validity range in [17]) are preferred to be used as basis of a diffusion approach, or for application in a correlations approach with its known drawbacks. The preference is explained by the consistency of the data, their larger time range (trend towards cubic rates at low temperature) and the availability of oxygen uptake results for the large total data base.

- Alternative use of the Cathcart-Pawel correlations [6] with the same corresponding procedures is acceptable, as well as the use of the combined Leistikow / Cathcart-Pawel data base.
- For pragmatic reasons an interim, linear interpolation procedure can be defined between the given low-temperature and the below addressed high-temperature range: Taking for orientation experimental results of Aly [16] (gained at 1823 and 1873 K and re-evaluated at KfK), the duplex scale formation gives rise to a gradual instead of a step-wise increase of reaction rates. An upper interpolation temperature of 1900 K seems acceptable. A refined procedure should be based on phase diagram and diffusion information and would thus need no arbitrary assumptions.
- The Prater-Courtright data or correlations [18] are the recommended choice for the high-temperature range above 1900 K. As counteraction against over-estimation an adequate steam supply limitation ought to be provided in the SA code calculation.
- For the high-temperature range no alternative is recommended for best-estimate application, despite the facts that the Baker-Just correlation [4] is less conservative in the range of Zry melting, and that the Urbanic-Heidrick correlations [13], contradicting all other published results, are still frequently considered.

3.2 Proposed interim application procedures

Since straightforward preparation of the input deck was urgent, some practical assistance and comments as given in the following were separately distributed in advance. The correlations from experimental programs of Prater and Courtright (HT range) and Leistikow et al. (or alternatively Cathcart and Pawel or a combination of the data sets of both groups), LT range, are recommended above; the combination alternative is not treated for simplicity. According to the above recommendations the technical proposal is to rely on a linear interpolation of the HT correlations and the LT correlations within a medium temperature range (MT range), representing the influence of the duplex scale in simplified manner. The recommended temperatures for the boundaries of the interpolation range are 1800 K (LT/MT) and 1900 K (MT/HT).

3.2.1 Formulation of the correlations

As already mentioned the form of the rate laws is defined to be $x^2=K*t$ (x=: mass gain $=\tau$, or the thickness of ZrO_2 scale $=\o$, α-Zr(O) layer $=\alpha$, or duplex layer ZrO_2+α-Zr(O) $=\xi$; t=time; K= rate coefficient to be given in temperature dependence). The formulations of the rate coefficients as defined by the experimentalists and as given in the literature are presented for reference. The coefficients deduced thereof are obtained by squaring or factor converting to get consistent sets and nomenclature.

Formulated to be applied in different codes the data are given in general form and require transformation according to special code conventions. So, each code user is responsible for the correct application of the given correlations in his special code!

To illustrate this argument the author refers to MELCOR, in which the weight of metal oxidised per unit surface area is calculated, whereas here the more basic mass gain (oxygen uptake) is presented. To avoid another trap it must be confirmed if the individual code uses correlations corresponding to the squared and integral form of the parabolic rate law (x^2=K*t, as used here) or to the differential form. Alternatively, the code calculation can be based on an integral or differential rate law containing the square-root-of-time and the correspondingly defined rate parameter, often termed δ: $x = \delta\sqrt{t}$.

3.2.2 Interpolation procedure

Linear interpolation between two correlations of Arrhenius type is understood to be obtained by a third correlation of the same type. It is defined by the two conditions of overcrossing at the boundaries of the given interpolation range between T_1 and T_2. For $T_1 > T_2$ the interpolation function crosses the HT correlation at T_1 and the LT correlation at T_2. Thus:

$$K^{MT}(T) = K_0^{MT}\exp\left(-Q^{MT}/T\right) \qquad (T_1 \geq T \geq T_2) \tag{1}$$

$$K^{HT}(T_1) = K_1 = K_0^{HT}\exp(-Q^{HT}/T_1) \tag{2}$$

$$K^{LT}(T_2) = K_2 = K_0^{LT}\exp(-Q^{LT}/T_2) \tag{3}$$

The parameters K_0^{MT} and Q^{MT} of (1) are determined from (2) and (3):

$$Q^{MT} = \frac{T_1 T_2}{T_1 - T_2}\ln\left(\frac{K_1}{K_2}\right) \tag{4}$$

$$\ln K_0 = \frac{T_1 \ln K_1 - T_2 \ln K_2}{T_1 - T_2} \tag{5}$$

Remarks:

Instead of using (5) the following equations are applied to obtain and check the consistency of K_o:

$$K_0^{MT} = K_1\exp(Q^{MT}/T_1); \; K_0^{MT} = K_2\exp(Q^{MT}/T_2); \qquad \text{(5a; 5b)}$$

Insertion into (1) and a straightforward transformation towards symmetry gives the interpolation condition in the following form:

$$T\ln K^{Int} = f_1(T) * T_1 \ln K_1 + f_2(T) * T_2 \ln K_2 \text{ with}$$

$$f_1(T) = \frac{T - T_2}{T_1 - T_2}, \quad f_2(T) = \frac{T_1 - T}{T_1 - T_2}, \text{ and } f_1(T) + f_2(T) = 1$$

3.2.3 Procedure for obtaining a correlation for the α-Zr(O) layer growth, missing in the Prater-Courtright set of correlations

The Prater-Courtright set of correlations is complete in the sense that the kinetic behaviour is fully determined by the given correlations. A correlation for the α-Zr(O) layer growth, which some user might need, can be obtained from the given ones. However, together with the resulting function the system is over-determined. Further, in the general case of differences in the temperature dependence of the layers growth, as in the present case, the deduced function would not be of strict Arrhenius type, but represented by a curve in the Arrhenius plot.

With the approximation procedure described below this complication is avoided at the expense of discrepancies due to the assumed Arrhenius type of the function: The curve is approximated by a straight line and the two fixed temperatures, used for fitting have to be arbitrarily chosen. In this sense a simple approximate solution is obtained by subtraction of the coefficients δ of the corresponding rate laws:

$$x = \delta_x \sqrt{t} \qquad \alpha = \xi - \varphi = (\delta_\xi - \delta_\varphi)\sqrt{t} = \delta_\alpha \sqrt{t}$$

ξ represents the ZrO_2+α-Zr(O) double layer, ø the ZrO_2 scale, and α the α-Zr(O) layer. In squared representation the corresponding formulation is:

$$K_\alpha = \delta_\xi^2 - 2\delta_\xi\delta_\varphi + \delta_\varphi^2 \neq K_\xi - K_\varphi$$

The parameters for α-Zr(O) layer growth, as determined from the Prater-Courtright correlations for double-layer and scale growth, are given in the respective section below. Prater and Courtright have restricted the validity of their double-layer correlation to an upper limit of 2173 K. Taking this value for orientation, the fitting was performed at 1800 and 2200 K. Thus, a fair representation of the original experimental results can be expected. Extrapolation by application to far higher temperatures would give increasing discrepancies.

With this procedure an Arrhenius correlation is “reconstructed” which can be used for application and interpolation purposes as described above.

3.2.4 Formulation of the proposed mass gain correlations

Prater, Courtright; T[K]=1783-2673, here proposed for HT range T>1900 K

$\delta_\tau^{\Pr Co,Zry} = 5.74 \exp(-13220/T)$ [g*cm^{-2}*s$^{-1/2}$]

$K_\tau^{\Pr Co} = 3.295 \cdot 10^1 \exp(-26440/T)$ [g^{2}*cm^{-4}*s^{-1}]

$K_\tau^{\Pr Co}(1900K) = 2.9803 \cdot 10^{-5} g^2 cm^{-4} s^{-1}$

Leistikow; T[K]=1173-1773, here proposed for LT range T<1800 K

$\delta_\tau^{Le} = 0.724 \exp(-10481/T)$ [g*cm^{-2}*s$^{-1/2}$]

$K_\tau^{Le} = 0.52418 \cdot \exp(-20962/T)$ [g^{2}*cm^{-4}*s^{-1}]

$K_\tau^{Le}(1800K) = 4.5907 \cdot 10^{-6} g^2 cm^{-4} s^{-1}$

Cathcart, Pawel; T[K]=1273-1773, alternative for LT range T<1800 K

$(\delta_\tau^{CaPa})^2/2 = 1.811 \cdot 10^{-1} \exp(-39940/RT)$ [g^{2}*cm^{-4}*s^{-1}]

$K_\tau^{CaPa} = 3.622 \cdot 10^{-1} \exp(-20100/T)$ [g^{2}*cm^{-4}*s^{-1}]

$K_\tau^{CaPa}(1800K) = 5.1207 \cdot 10^{-6} g^2 cm^{-4} s^{-1}$

Interpolation function between Prater-Courtright and Leistikow correlations (proposed for MT range T[K]=1800-1900):

$K_\tau^{\Pr/Le} = 1.2508 \cdot 10^{10} \exp(-63974/T)$ [g^{2}*cm^{-4}*s^{-1}]

Interpolation function between Prater-Courtright and Cathcart-Pawel correlations (alternative for MT range T[K]=1800-1900):

$K_{\tau}^{\Pr/Ca} = 1.7498 \cdot 10^{9} \exp(-60237/T)$ [g^2*cm^{-4}*s^{-1}]

3.2.5 Formulation of the proposed ZrO_2 scale growth correlations

Prater, Courtright; T[K]=1783-2673, here proposed for HT range T>1900 K

$\delta_{\varphi}^{\Pr Co,Zry} = 5.46 \exp(-14210/T)$ [cm*$s^{-1/2}$]

$K_{\varphi}^{\Pr Co} = 2.98116 \cdot 10^{1} \exp(-28420/T)$ [cm^2*s^{-1}]

$K_{\varphi}^{\Pr Co}(1900K) = 5.5116 \cdot 10^{-6} cm^2 s^{-1}$

Leistikow; T[K]=1173-1773, here proposed for LT range T<1800 K

$(\delta_{\varphi}^{Le})^2/2 = 3.91 \cdot 10^{-2} \exp(-40164/RT)$; (R=1.987cal*K^{-1}*mol^{-1}) [cm^2*s^{-1}]

$K_{\varphi}^{Le} = 7.82 \cdot 10^{-2} \exp(-20214/T)$ [cm^2*s^{-1}]

$K_{\varphi}^{Le}(1800K) = 1.037 \cdot 10^{-6} cm^2 \cdot s^{-1}$

Cathcart, Pawel; T[K]=1273-1773, alternative for LT range T<1800 K

$(\delta_{\varphi}^{CaPa})^2/2 = 1.126 \cdot 10^{-2} \exp(-35890/RT)$; (R=1.987cal*K^{-1}*mol^{-1}) [cm^2*s^{-1}]

$K_{\varphi}^{CaPa} = 2.252 \cdot 10^{-2} \exp(-18062/T)$ [cm^2*s^{-1}]

$K_{\varphi}^{CaPa}(1800K) = 9.877 \cdot 10^{-7} cm^2 \cdot s^{-1}$

Interpolation function between Prater-Courtright and Leistikow correlations (proposed for MT range T[K]=1800-1900):

$K_{\varphi}^{\Pr/Le} = 2.0078 \cdot 10^{12} \exp(-75793/T)$ [cm^2*s^{-1}]

Interpolation function between Prater-Courtright and Cathcart-Pawel correlations (alternative for MT range T[K]=1800-1900):

$K_{\varphi}^{\Pr/Ca} = 4.8253 \cdot 10^{12} \exp(-77459/T)$ [cm^2*s^{-1}]

3.2.6 Formulation of the proposed ZrO_2+α-Zr(O) double layer growth correlations

Prater, Courtright; T[K]=1783-2173, here proposed for HT range T>1900 K

$\delta_{\xi}^{\Pr Co,Zry} = 2.05 \exp(-11550/T)$ [cm*$s^{-1/2}$]

$K_{\xi}^{\Pr Co} = 4.2025 \exp(-23100/T)$ [cm^2*s^{-1}]

$K_{\xi}^{\Pr Co}(1900K) = 2.2049 \cdot 10^{-5} cm^2 s^{-1}$

Leistikow; T[K]=1173-1773, here proposed for LT range T<1800 K

$(\delta_{\xi}^{Le})^2/2 = 8.30 \cdot 10^{-1} \exp(-43885/RT)$; (R=1.987cal*K^{-1}*mol^{-1}) [cm^2*s^{-1}]

$K_{\xi}^{Le} = 1.66 \exp(-22086/T)$ [cm^2*s^{-1}]

$K_{\xi}^{Le}(1800K) = 7.786 \cdot 10^{-6} cm^2 \cdot s^{-1}$

Cathcart, Pawel; T[K]=1273-1773, alternative for LT range T<1800 K

$(\delta_{\xi}^{CaPa})^2/2 = 3.412 \cdot 10^{-1} \exp(-41700/RT)$; (R=1.987cal*K^{-1}*mol^{-1}) [cm^2*s^{-1}]

$K_{\xi}^{CaPa} = 6.824 \cdot 10^{-1} \exp(-20986/T)$ [cm^2*s^{-1}]

$K_{\xi}^{CaPa}(1800K) = 5.897 \cdot 10^{-6} cm^2 \cdot s^{-1}$

Interpolation function between Prater-Courtright and Leistikow correlations (proposed for MT range T[K]=1800-1900):

$K_{\xi}^{Pr/Le} = 3.02479 \cdot 10^3 \exp(-35600/T)$ [cm^2*s^{-1}]

Interpolation function between Prater-Courtright and Cathcart-Pawel correlations (alternative for MT range T[K]=1800-1900):

$K_{\xi}^{Pr/Ca} = 4.49867 \cdot 10^5 \exp(-45104/T)$ [cm^2*s^{-1}]

3.2.7 Formulation of the proposed α-Zr(O) layer growth correlations

Prater, Courtright; deduced from original data for ZrO_2 scale and ZrO_2+α-Zr(O) double layer growth according to above described procedure (approximation in Arrhenius form), here proposed for HT range T>1900 K

$\delta_{\alpha}^{PrCo,Zry} = 2.26717 \cdot 10^{-2} \exp(-5126/T)$ [cm*s$^{-1/2}$]

$K_{\alpha}^{PrCo} = 5.14006 \cdot 10^{-4} \exp(-10252/T)$ [cm^2*s^{-1}]

$K_{\alpha}^{PrCo}(1900K) = 2.33135 \cdot 10^{-6} cm^2 s^{-1}$

Leistikow; T[K]=1173-1773, here proposed for LT range T<1800 K

$(\delta_{\alpha}^{Le})^2/2 = 2.54 \cdot 10^{-1} \exp(-43561/RT)$; (R=1.987cal*K^{-1}*mol^{-1}) [cm^2*s^{-1}]

$K_{\alpha}^{Le} = 5.08 \cdot 10^{-1} \exp(-21923/T)$ [cm^2*s^{-1}]

$K_{\alpha}^{Le}(1800K) = 2.611779 \cdot 10^{-6} cm^2 \cdot s^{-1}$

Cathcart, Pawel; T[K]=1273-1773, alternative for LT range T<1800 K

$(\delta_{\alpha}^{CaPa})^2/2 = 7.615 \cdot 10^{-1} \exp(-48140/RT)$; (R=1.987cal*K^{-1}*mol^{-1}) [cm^2*s^{-1}]

$K_{\alpha}^{CaPa} = 1.523 \exp(-24227/T)$ [cm^2*s^{-1}]

$K_{\alpha}^{CaPa}(1800K) = 2.17439 \cdot 10^{-6} cm^2 \cdot s^{-1}$

Interpolation function between Prater-Courtright and Leistikow correlations (proposed for MT range T[K]=1800-1900):

$K_{\alpha}^{Pr/Le} = 3.08617 \cdot 10^{-7} \exp(+3842/T)$ [cm^2*s^{-1}]

Interpolation function between Prater-Courtright and Cathcart-Pawel correlations (alternative for MT range T[K]=1800-1900):

$$K_{\alpha}^{\mathrm{Pr}/Ca} = 8.1759 \cdot 10^{-6} \exp(-2384/T) \qquad [\mathrm{cm}^2 * \mathrm{s}^{-1}]$$

4. Future demands

4.1 Critical examination of experimental information and modelling

Progress in understanding and accounting of accident conditions and materials behaviour is clearly indicated in consecutive State-of-the-art Reports (SOAR´s). So the OECD Nuclear Energy Agency, Committee on the Safety of Nuclear Installations (CSNI), Principal Working Group 2, edited a SOAR in 1991, worked out by a group of authors [23]. The chapter 4.3 (Status of the Data-Base) and the Summary may serve for reference. In an update, covering available information up to June 1993, intended to help to identify priorities of a CEC funded Re-inforced Concerted Action, reviews of recent experimental programs and the status of assessment of main codes were documented, modelling needs identified and recommendations given. Concerning model improvements, considered necessary concerning oxidation and related cladding performance, the analysis of the range of uncertainties of the isothermal correlations used in the codes, the prediction of the onset of oxidation-induced temperature escalation and the description of cladding failure were mentioned.

In 1996 the European Commission issued a SOAR of equally high value on In-vessel core degradation in LWR severe accidents [24]. A literature survey on the oxidation behaviour of Zr-Nb alloys, in comparison to those of Western type, facilitates modelling in this field. In the chapter “Identification of Modelling Needs” improvements in the treatment of phenomena were seen. In the chapter “Conclusions and Recommendations” a diminishing distinction between “system-level” and “detailed deterministic” codes was mentioned. It was argued that further improvements in the future would depend therefore more on the availability of realistic materials properties data.

The author supports most of the above cited statements, but disagrees especially in the last-mentioned argument, if applied to the field of zirconium oxidation kinetics. Instead it is repeated that a fund of experimental information is available, mostly since many years, whereas its application in most SA codes remains in a preliminary or inadequate state. The intention of this paper is to put impetus on the task to improve SA code performance by promoting the choice of the best-adequate correlations for application in codes. This will replace the arbitrariness of user-defined options by an agreed data base in various codes, and will thus facilitate comparison of different codes with respect to other features. However, this will be only a first step (Fig. 8), others have to follow, as mentioned below.

The opportunity to initiate this action within COLOSS is appreciated, since this project provided ideal communication between the fields of experimental versus analytical work and on separate-effects versus integral scale. In the past lack of communication and mutual understanding of the possibilities and limitations in the experimental and the analytical fields might have delayed necessary data implementation. Code verification deserves extra support in dedicated future projects.

4.2 Future demands

The paper was concentrated on the oxidation kinetics of alloys of Zr-Sn type and has not considered those of Zr-Nb type for which also much experimental information is available. The author is not sufficiently informed to give a statement on the choice of correlations to be preferred and on additional experimental information, possibly required for highest temperatures. One can expect close similarities in most aspects of the behaviour, so that many arguments in this paper should be relevant. But a separate action would be appreciated, as the importance of this alloy family is increasing in the Western countries as well. This leads over to the task to keep pace with actual cladding alloy development and fuel element design improvements in modelling the SA performance of Nuclear Power Plants.

Some of the drawbacks and limitations of a correlations approach compared to a diffusion system approach have been explained in the text, so that it is sufficient here to summarise the following items: Correlations are strictly applicable only for a semi-infinite system and give thus a fair representation only of sufficiently thick specimens or over correspondingly limited time scales ($\tau \sim L^2/D$, L=thickness, D=diffusion coefficient). Related discrepancies follow for the consumption of β-Zr phase matrix and total conversion to ZrO_2. Correlations are not applicable to gas-phase-limited steam supply and scale dissolution in contact to metal and complete isolation from steam (“chemical thinning”), cases requiring a separate approach. Important underestimation of temperature-transient scale growth by correlations approach is reported [22]. Further, correlations are a weak base for modelling of cladding embrittlement and mechanical behaviour in general. Facing all arguments one can speculate that every ambitious SA code improvement in the future will include replacement of the correlations approach by the diffusion approach. In this task the adequate fundament of kinetic and phase diagram data will be equally important.

It became clear that improvement of the treatment of oxidation kinetics, as supported by this paper, is only one of a group of fields in which future improvements are necessary. One of them, gas phase steam transfer and related supply limitation has been considered above. Equally important is the definition of clad failure criteria on physical basis, instead of their use in the sense of “trimming screws”. Failure criteria are interpreted to focus a range of real materials behaviour variation into an image of abrupt mathematical actions. Since those determine the limits of undisturbed fuel element geometry towards degradation and melt relocation, it is important to find consensus and to avoid arbitrary user-defined definitions in different SA codes.

The actual status of development of a model for treatment of the oxidation of melts by Veshchunov et al. [25] shows promising progress in a most important field. Again, it was found that an approach on basis of a simple correlation is not sufficient. This work is of high value for the QUENCH activity at FZK, with respect to the experimentally observed dramatic hydrogen release from bundles, quenched from conditions, in which melt release and oxidation have taken place. SA scenarios, in which more severe fuel element degradation occurs and melt pool oxidation persists, will take full profit from this model development.

A promising action initiated within COLOSS is the approach to identify risk-relevant parameters and their ranking according to priority with respect to hydrogen production risk, B_4C oxidation related gas release risk, and corium relocation related vessel failure risk. The combined feedback of experience from plant calculations, performed within the PAG, is expected to be valuable for future projects.

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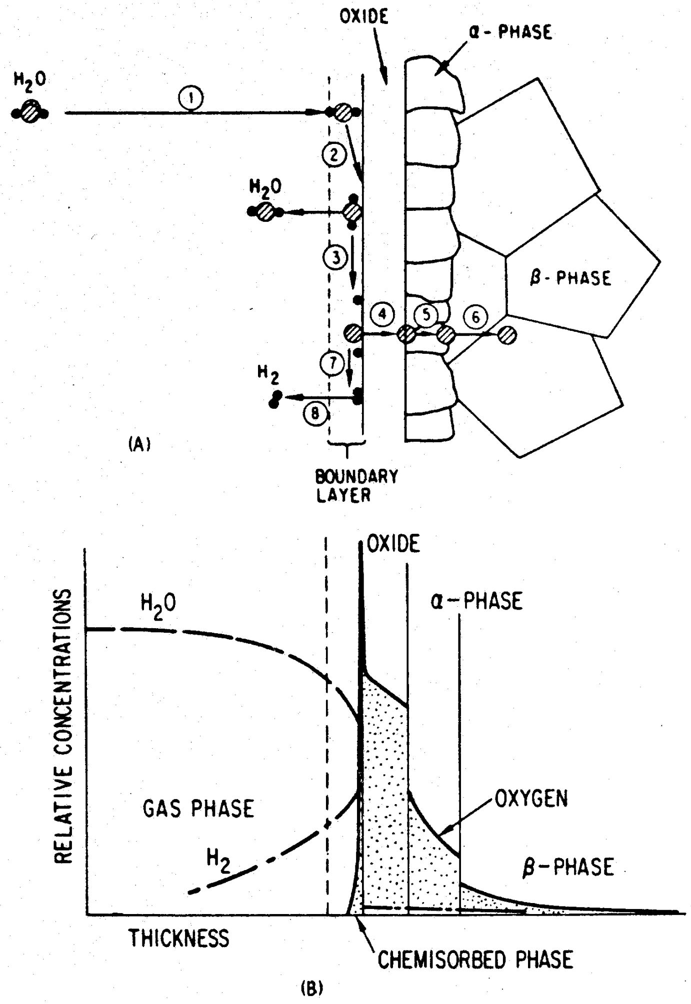

Fig. 1.

Schematic Illustrations of (A) the Physical Processes during Zircaloy-Steam Oxidation and (B) the Corresponding Relative Concentration Gradients of Reacting Species across the Phase Layers. The elementary steps are gaseous diffusion of steam (1), chemisorption of steam (2), dissociation into oxygen and hydrogen (3), diffusion of oxygen in the oxide (4), alpha (5), and beta (6) phases, recombination of hydrogen (7), desorption of gaseous hydrogen (8).

Fig. 1: Scheme of the diffusion system Zircaloy/steam (H.M. Chung, G.R. Thomas; “The Retarding Effect of Hydrogen on Zircaloy Oxidation”. NSAC-29, 1981)

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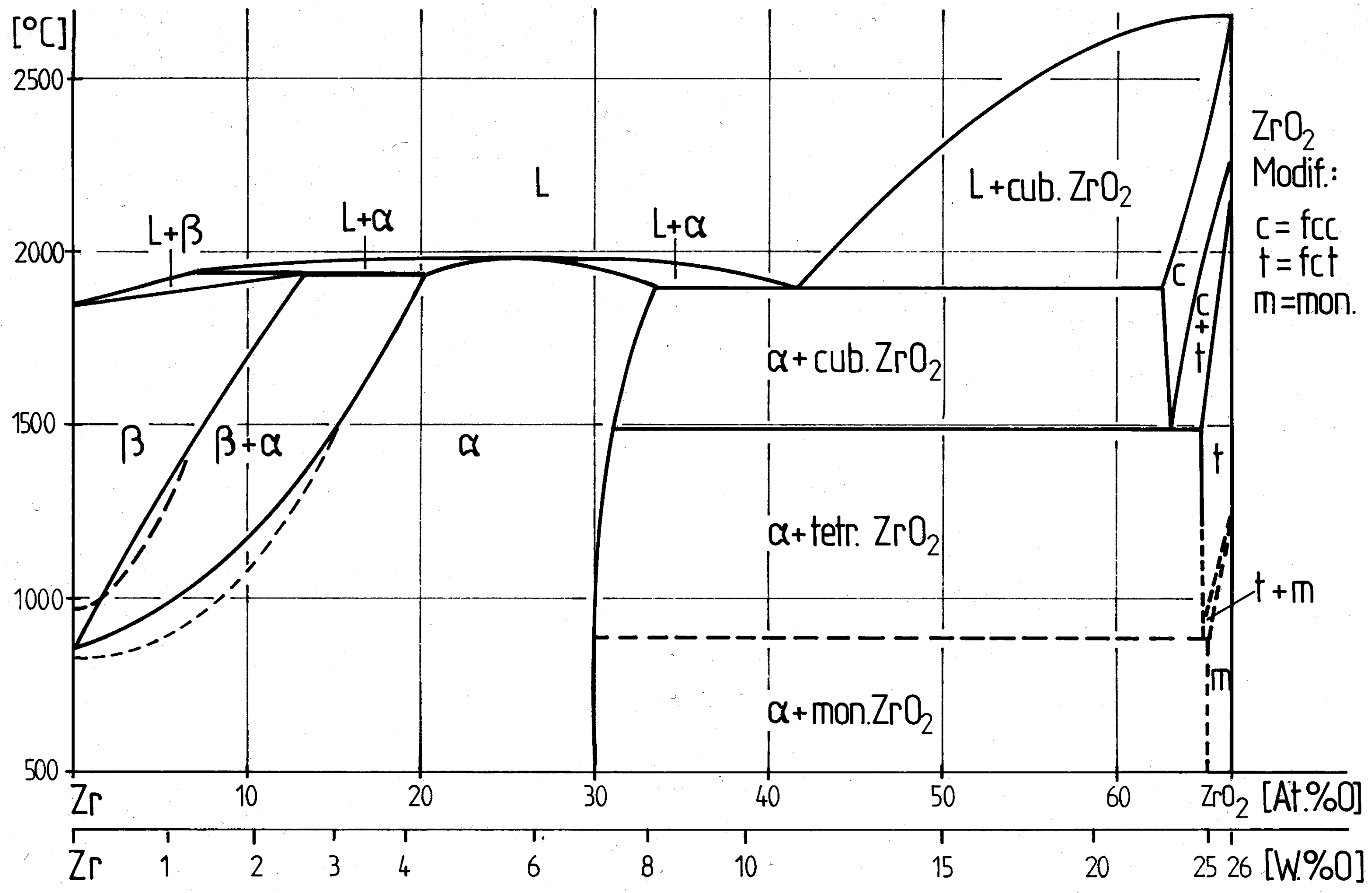
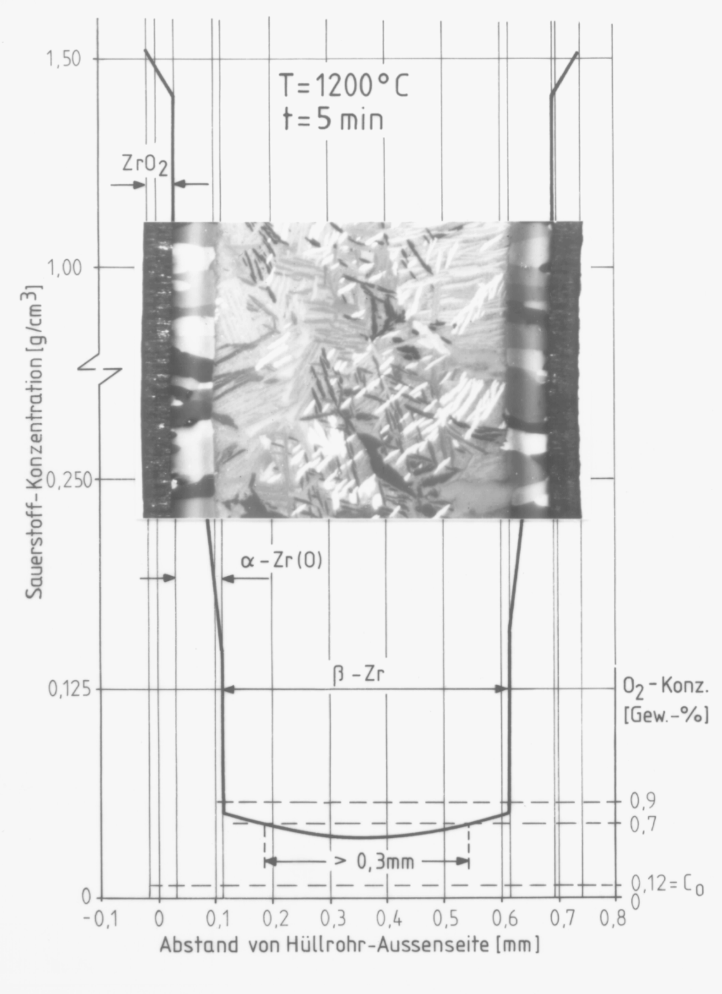


Fig. 2: Combination of Zr-O phase diagram information; (KfK, 1978, sources Gebhard et al., Ruh et al. (Zr), Kassner et al. (Zry), given in Ref. [9,])



A) Presently valid Embrittlement Criteria

Limitation of the maximum cladding temperature and the maximum. percentage of calculated oxidative cladding wall conversion:

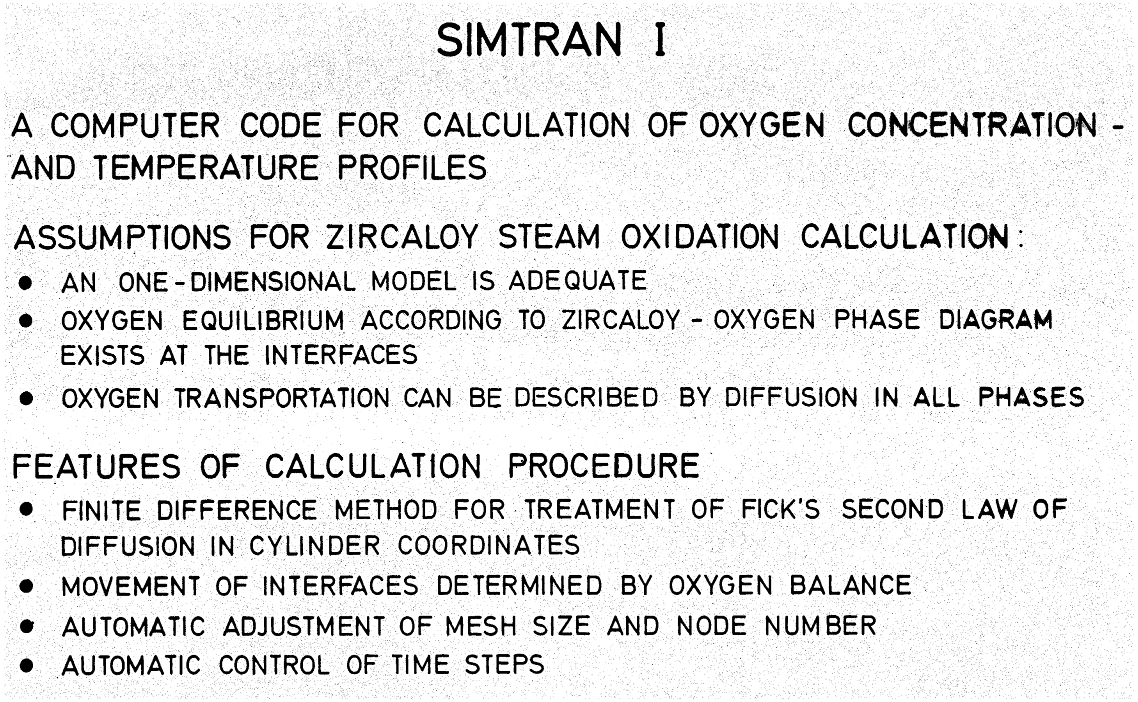
- T_{max} </= 1200 °C
- wall conversion Δs </= 17 % $s_{orig.}$

B) Proposal by ANL

Definition of a residual minimum thickness of sufficiently ductile wall:

- with respect to thermal shock during reflood:
  s(0.9 wt.% O_2) > 0.1 mm
- with respect to handling, transport and interim storage:
  s(0.7 wt.% O_2) > 0.3 mm

Fig. 3: Synopsis of presently valid and new Embrittlement Criteria, proposed by Chung and Kassner (Ref. [5]), right side, and the type of required information, left side: An oxygen concentration profile through the wall of a double-sided oxidised Zry tube, calculated with SIMTRAN (Ref. [8]) is overlaid by a cross section micrograph of a specimen after oxidation test at KfK, showing good representation of layers growth by the code (S. Leistikow et al., 1980, unpublished illustration)



SIMTRAN I

A COMPUTER CODE FOR CALCULATION OF OXYGEN CONCENTRATION - AND TEMPERATURE PROFILES

ASSUMPTIONS FOR ZIRCALOY STEAM OXIDATION CALCULATION:

- AN ONE-DIMENSIONAL MODEL IS ADEQUATE
- OXYGEN EQUILIBRIUM ACCORDING TO ZIRCALOY - OXYGEN PHASE DIAGRAM EXISTS AT THE INTERFACES
- OXYGEN TRANSPORTATION CAN BE DESCRIBED BY DIFFUSION IN ALL PHASES

FEATURES OF CALCULATION PROCEDURE

- FINITE DIFFERENCE METHOD FOR TREATMENT OF FICK'S SECOND LAW OF DIFFUSION IN CYLINDER COORDINATES
- MOVEMENT OF INTERFACES DETERMINED BY OXYGEN BALANCE
- AUTOMATIC ADJUSTMENT OF MESH SIZE AND NODE NUMBER
- AUTOMATIC CONTROL OF TIME STEPS

CONNECTION BETWEEN ZIRCALOY-OXYGEN PHASE DIAGRAM AND OXYGEN CONCENTRATION PROFILE

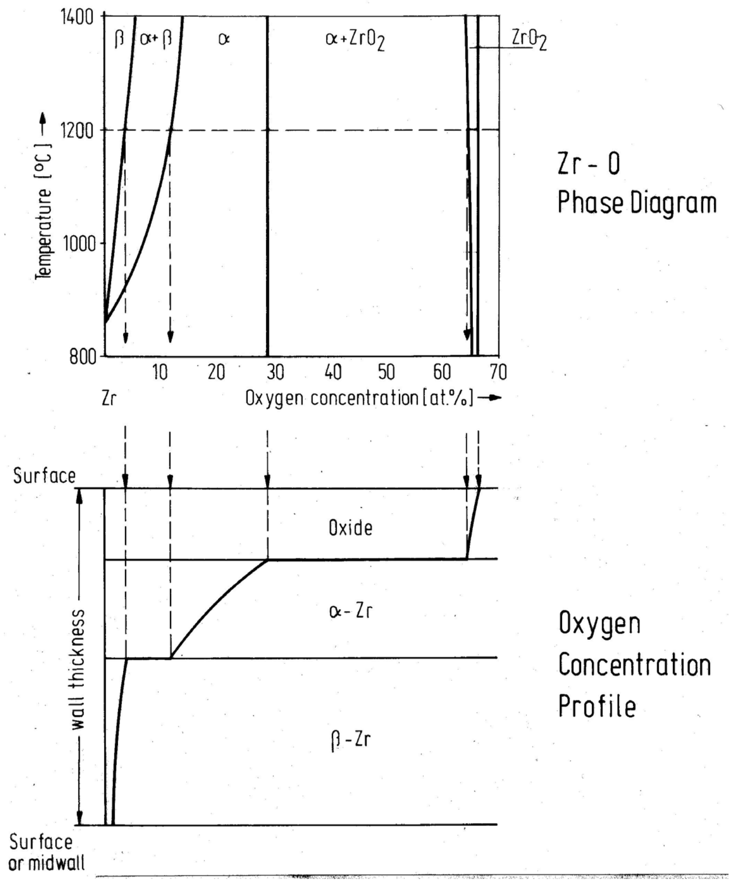
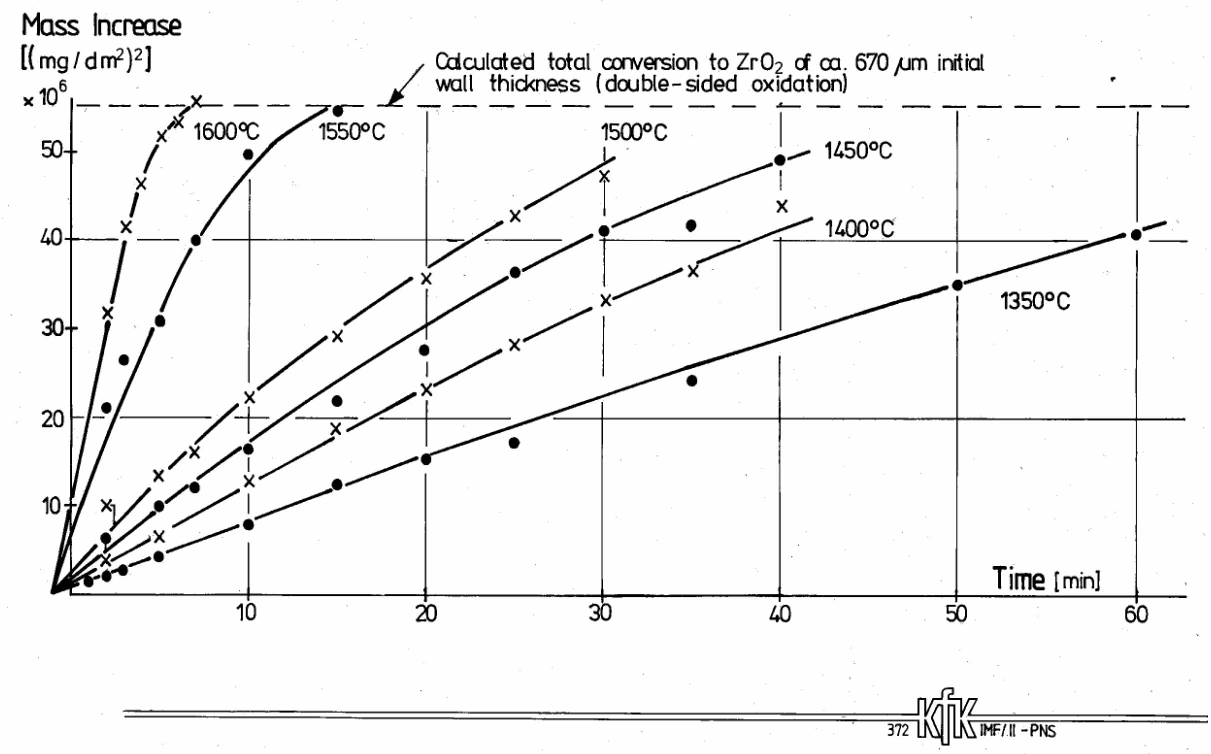
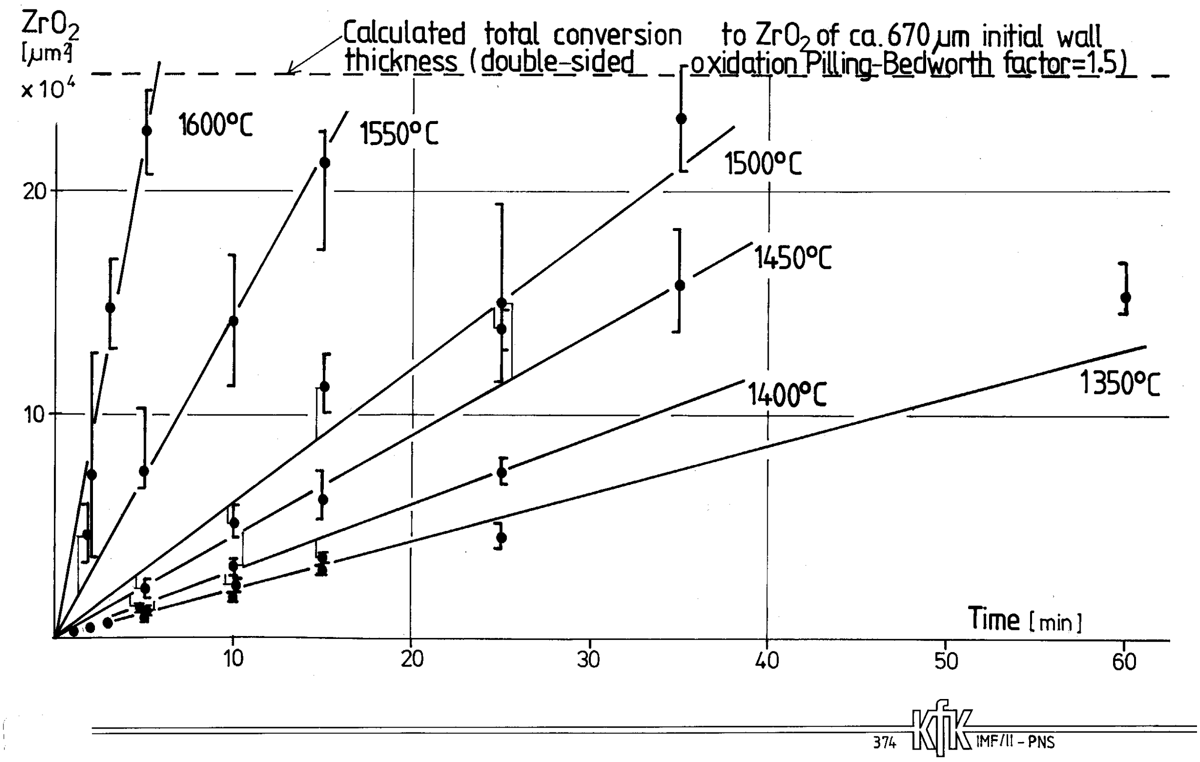


Fig. 4: Features of the code SIMTRAN, developed by S. Malang at ORNL, Ref. [8]. Illustrations from S. Malang, G. Schanz, OECD-CSNI Meeting Spatind, Norway, 1976

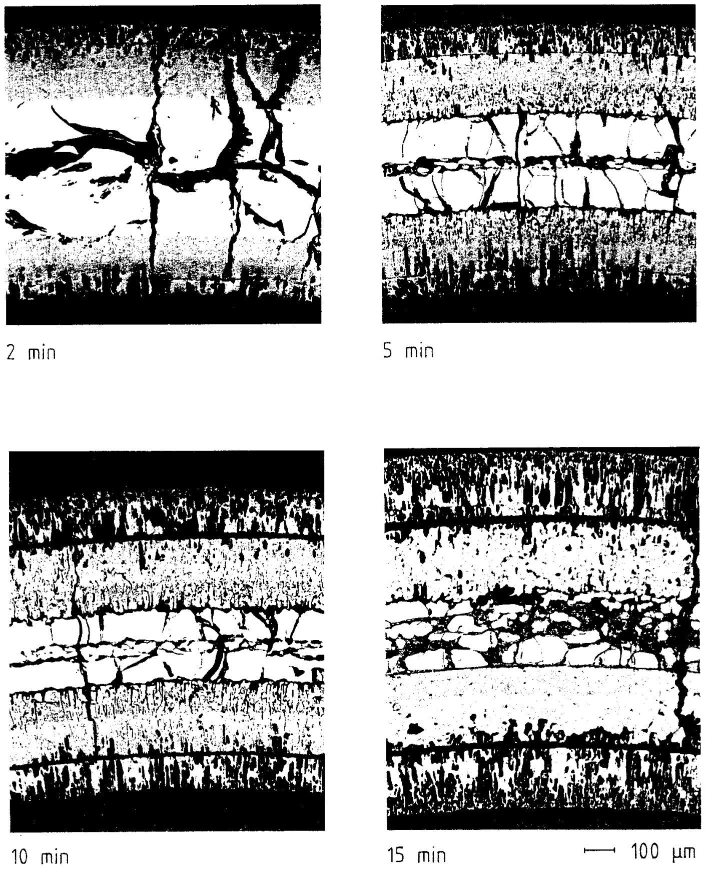


Mass-Increase during Zircaloy-4/Steam HT Oxidation at 1350–1600°C in Parabolic Representation



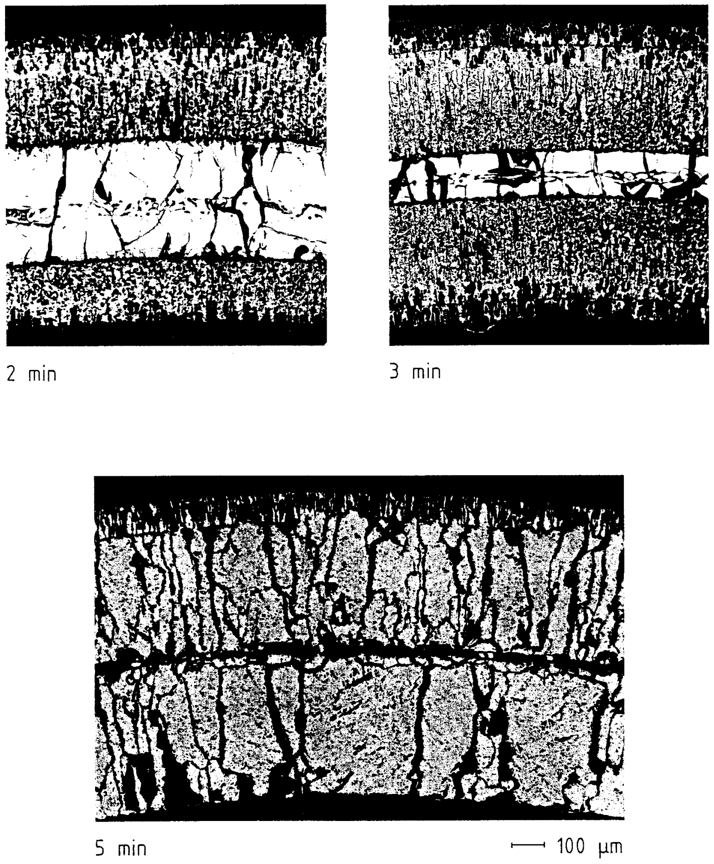
ZrO_2 Scale Growth during Zircaloy-4/Steam HT Oxidation at 1350–1600°C in Parabolic Representation

Fig. 5: Parabolic evaluation of mass gain and ZrO_2 scale growth kinetics (Ref. [17])



352 IMF/II

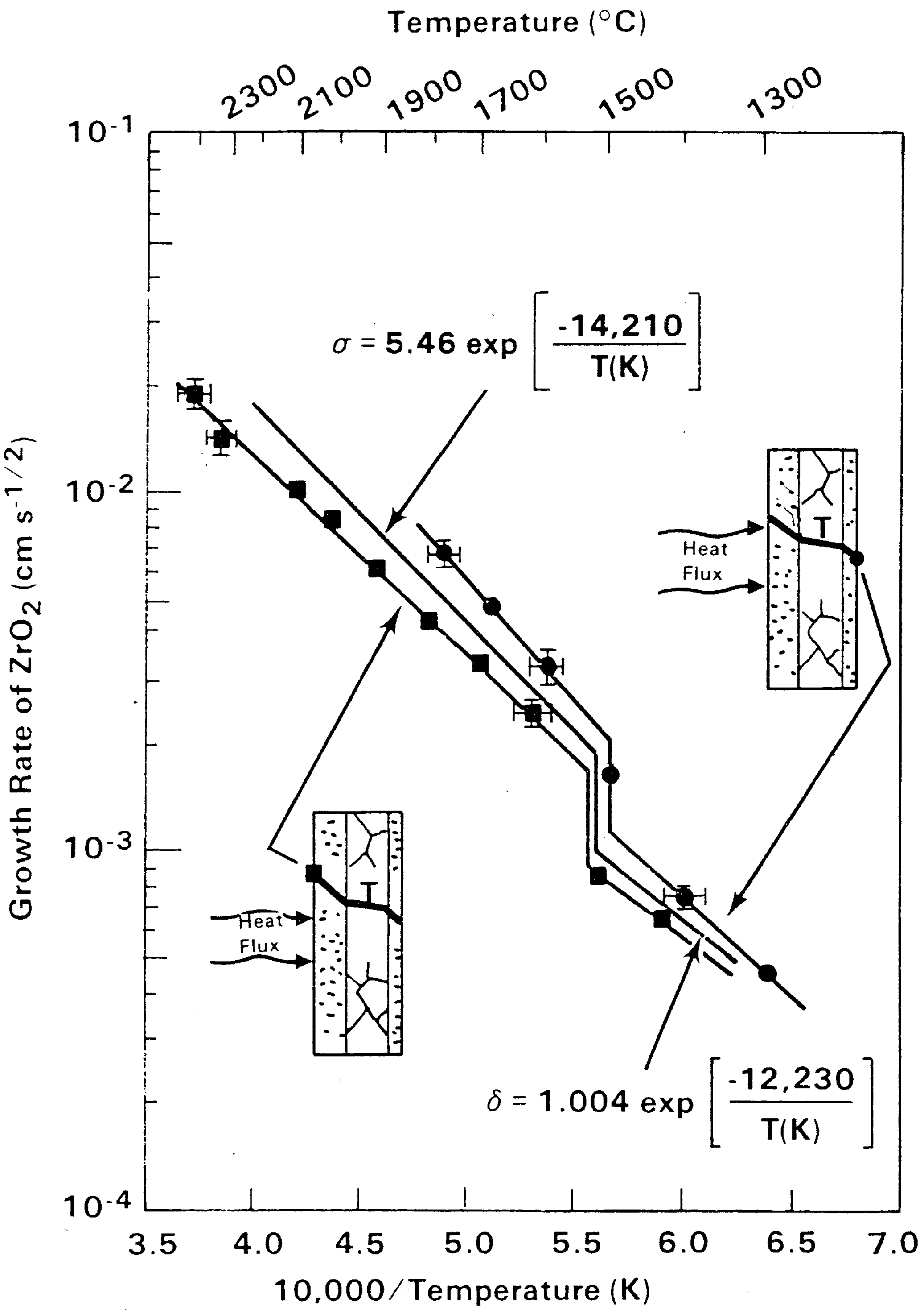
Isothermal Zircaloy-4 / Steam Oxidation
(1550°C, 2 min - 15 min)



353 IMF/II

Isothermal Zircaloy-4 / Steam Oxidation
(1600°C, 2 min - 5 min)

Fig. 6: Cross sections of tube specimens after double-sided oxidation at 1550 and 1600 °C. (S. Leistikow et al., unpubl. illustr., 1983)



Parabolic Rate Constants for Oxide Layer Growth.

The intermediate curve represents the best estimate "true" isothermal conditions.

Fig. 7: Correlations as given by Prater and Courtright for the scale growth kinetics in two temperature regimes, together with the evaluation procedure (Ref. [18]).

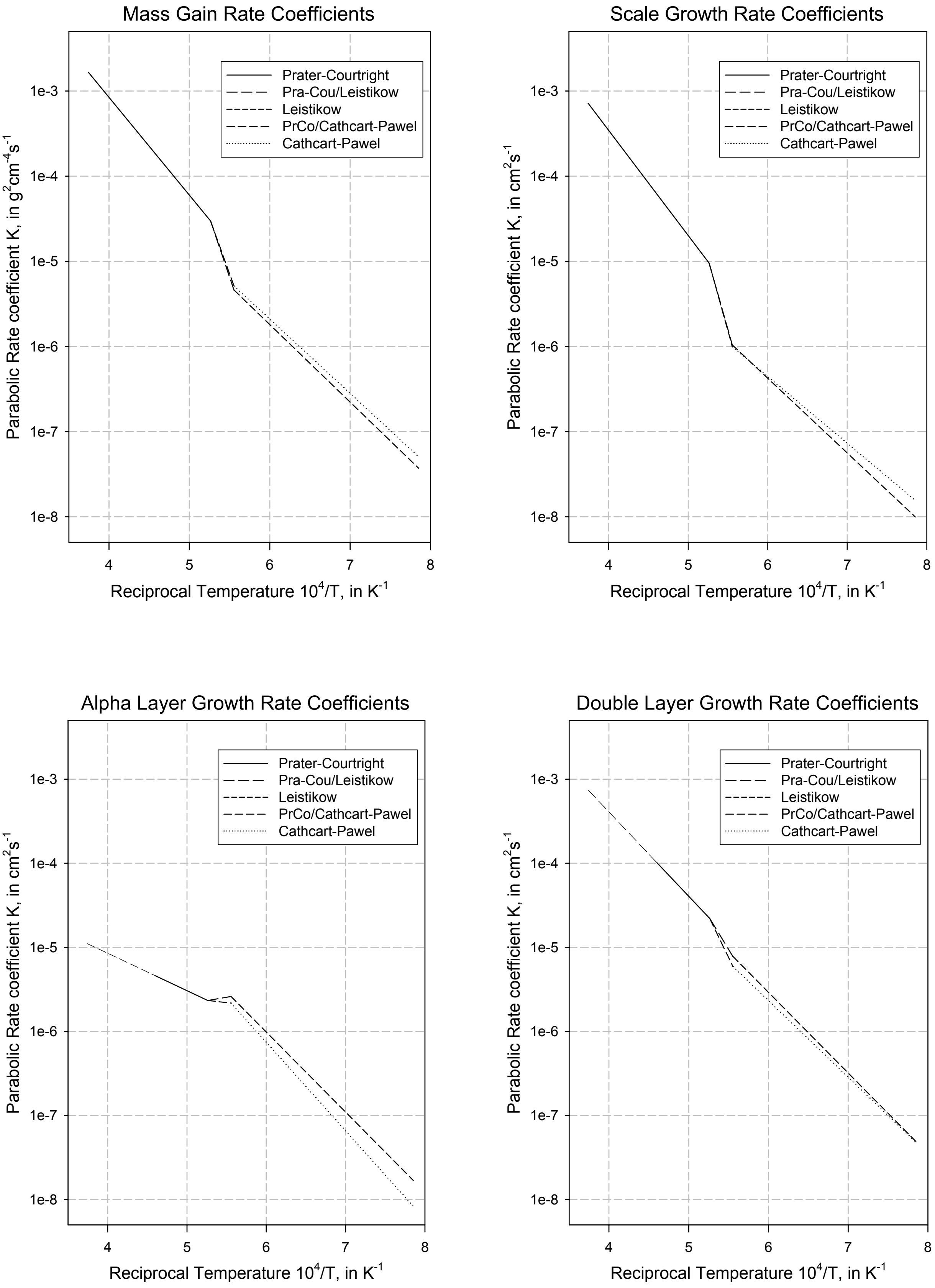


Fig. 8: Comparison of recommended correlations for Zircaloy-4 / steam oxidation