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# Embrittlement of ZrNb1 at room temperature after high-temperature oxidation in steam atmosphere

*Dedicated to Professor Werner Oldekop on his 65th birthday*

The ductility of ZrNb1 claddings after exposure to steam between 700 and 1000 °C was determined by ring compression tests at room temperature and compared with the ductility behaviour of Zircaloy. The ductility of ZrNb1 is quickly reduced by steam exposure. Complete embrittlement of ZrNb1 is reached at a relative equivalent oxide-layer thickness of 5%, in contrast to Zircaloy, where a relative thickness of 17% is necessary to produce complete embrittlement. The different behaviour of the two alloys is caused by higher oxygen uptake and a more homogeneous oxygen distribution in ZrNb1 after cooling. Between 950 and 1000 °C, there is an additional effect of high hydrogen absorption. Validity of the 17% criterion for ZrNb1 can no longer be taken for granted in view of these experimental findings.

*Versprödung von ZrNb1 bei Raumtemperatur durch Hochtemperaturoxidation in Wasserdampfatmosphäre. Hüllrohre aus ZrNb1 und Zircaloy wurden einer Wasserdampfatmosphäre von 700 bis 1000 °C ausgesetzt; anschließend wurde ihre Zähigkeit in Ringdruckversuchen bei Zimmertemperatur überprüft. Wasserdampf führt zu einer starken Abnahme der Zähigkeit von ZrNb1. Schon bei einer äquivalenten Oxidschichtdicke von 5% tritt vollständige Versprödung ein. Bei Zircaloy dagegen ist dies erst bei einer äquivalenten Oxidschichtdicke von 17% der Fall. Das verschiedene Verhalten beider Legierungen beruht darauf, daß ZrNb1 mehr Sauerstoff aufnimmt und dieser nach der Abkühlung homogener verteilt ist als im Fall von Zircaloy. Zwischen 950 und 1000 °C wirkt eine starke Absorption von Wasserdampf im gleichen Sinn. Eine Gültigkeit des 17%-Kriteriums für ZrNb1 kann angesichts dieser Ergebnisse nicht mehr angenommen werden.*

## 1 Introduction

During a loss-of-coolant accident in a light water reactor the geometry of the reactor core must remain unchanged and the possibility of unloading the core must be maintained. A sufficient residual ductility of the cladding material is required in the low-temperature range so that the fuel elements can withstand the stress during core flooding and during unloading and transport manipulations.

Present legal specifications ensure such a behaviour only indirectly by limiting the maximum permissible oxide-layer thickness. This criterion is based on investigations by *Hobson* and *Rittenhouse* on embrittlement of Zircaloy by high-temperature oxidation in steam [1]. A complete embrittlement of

Zircaloy was found after double-sided oxidation if the equivalent oxide-layer thickness, calculated from the temperature-time relation according to Baker-Just's relation (quoted, e.g., in [2]), was equal to, or greater than, 17 per cent of the original cladding thickness. The 17 per cent criterion was introduced as one of the emergency core cooling system acceptance criteria in the United States.

Later it was found that a criterion which had been defined in such a way conservatively limited the behaviour at simulated core flooding and as regards sufficient fracture toughness [2–4].

In many countries, the 17 per cent criterion was introduced, at most slightly modified, into the national regulations for loss-of-coolant accidents. However, a well-defined relationship between oxide-layer thickness and embrittlement was not always found. Thus *Kawasaki* et al. [5] stated the influence of the oxidation temperature beside the oxide-layer thickness, whereas according to *Furuta* et al. [6–8] embrittlement does not correlate with the uptake of oxygen but rather with the uptake of hydrogen. Therefore, other authors [9–13] proposed the use of other criteria for limiting the permissible oxidation. Preferably, they considered the oxygen concentration in the metallic matrix as essential.

All these results were achieved for the alloy system Zircaloy. In this paper it is investigated to which extent the 17 per cent criterion is applicable to the ZrNb1 claddings which are used in VVER-type reactors. It depends on the results of these investigations whether the criterion has to be taken into con-
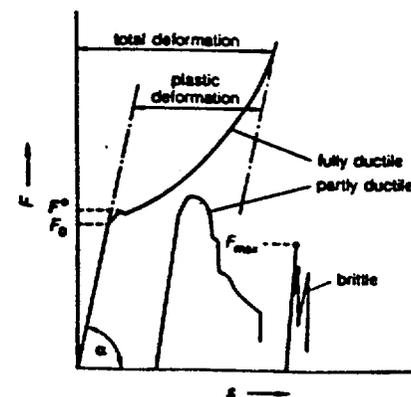


Fig. 1. Relationship between force F and relative displacement s during compression tests of materials with different ductilities. $F_{max}$ maximum loading, $F_0$ beginning of plastic deformation, $F^*$ yield point
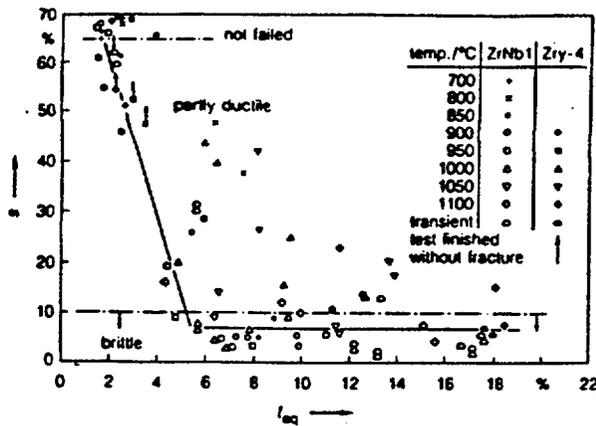
Fig. 2. *Dependence of the relative displacement s on the relative equivalent oxide-layer thickness $t_{eq}$ during ring compression tests of claddings of ZrNb1 and Zircaloy-4 after steam oxidation*

sideration in the frame of legal regulations for VVER-type plants.

## 2 Experimental

Experimental investigations were carried out with pressurized water reactor fuel claddings made of ZrNb1 (USSR) and Zry-4 (Sandvik, Sweden). The ZrNb1 tubes (nominal dimensions 9.1 mm diameter × 0.7 mm) and the Zry-4 tubes (nominal dimensions 10.75 mm diameter × 0.72 mm) were cut into 8 mm long sections. Samples of other lengths were used for reference investigations (weight gain and microstructure).

The alloys were used in their original state. After degreasing and pickling in aqueous HF/HNO₃ solution the following procedure were carried out: The samples were isothermally annealed in a tubular furnace under flowing steam (flow rate 90 ml/h) in the temperature range 700 to 1100°C for various times and subsequently quenched in water or cooled in air. The steam was produced in an external steam generator and preheated before entering the tubular furnace.

Reference investigations were carried out after temperature-transient steam oxidation (heating at a rate of 12 K/min up to 1200°C, quenching by premature sampling or cooling at a rate of 15 K/min), after homogeneous oxygen loading and after hydrogenation.

The ductility was determined by radial compression tests with tube sections at room temperature. The ring compression test is a frequently used method for evaluation of cladding embrittlement [2, 6–9]. Its special advantage is its simplicity. Yield stress, fracture stress, elastic modulus and deformation at break can be determined by this method [14]. Typical stress-strain diagrams for brittle, partly ductile, and fully ductile materials as well as the characteristic measuring data are shown in Fig.1.

All samples were visually investigated and their weight gain was determined. The structure was evaluated by metallographically prepared cross sections. In addition, the thickness of oxide and alpha layers and the radial profile of microhardness (at a load of 245 N) were measured, the hydrogen concentration was determined by vacuum extraction, and the fracture surface was investigated with a micro probe and by scanning electron microscopy.

## 3 Results

The dependence of the relative displacement on the relative equivalent oxide-layer thickness $t_{rel}$ is shown in Fig. 2. The latter was calculated from the weight gain $\Delta m$ with the formula

$$t_{eq} = \frac{A(Zr)}{M(O_2)\,\rho\,(Zr)\,O\,t_0} \cdot \Delta m \qquad (1)$$

where
$A(Zr)$ is the atomic weight of Zr,
$\rho(Zr)$ is the density of Zr,
$M(O_2)$ is the molecular weight of $O_2$,
$O$ is the surface,
$t_0$ is the initial wall thickness of the cladding.

The ductility reduction with increasing oxide-layer thickness can be seen in Fig.2. It corresponds with the expected behaviour. While the ductility of Zircaloy was reduced slowly, there was a rapid decrease for ZrNb1, which led to complete embrittlement at a relatively small oxide-layer thickness of about 5%. In addition, the effect of oxidation temperature cannot be disregarded for ZrNb1. Oxidation at 950 and 1000°C was especially critical.

The well-known three-layer structure formed during high-temperature oxidation, consisting of oxide, oxygen-stabilized $\alpha$ phase and $\beta$-backtransformed $\alpha'$ matrix, can be proved by fractographic investigation of the fracture surface. At deformation, the oxide and $\alpha$ layers will in any case brittly tear. So the sample ductility is determined by the ability of the $\alpha'$ ma-
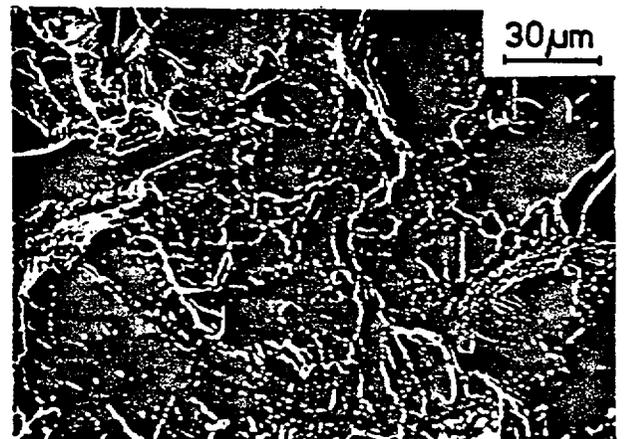


Fig. 3. *Comparison of fracture surfaces in the $\alpha'$ matrix. Left: Zircaloy-4, oxidation by steam at 1100°C for 30 min. Right: ZrNb1, oxidation by steam at 1050°C for 30 min. Pictures taken by scanning electron microscopy*
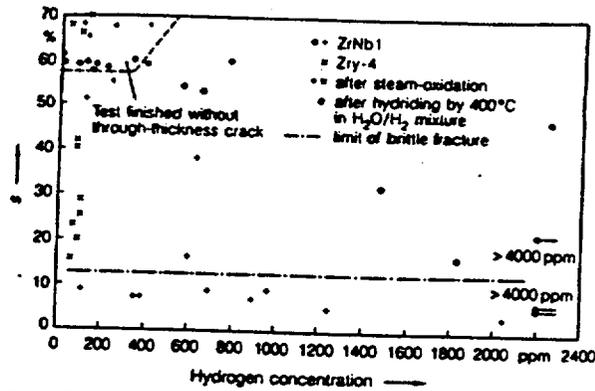
Fig. 4. Effect of hydrogen concentration on room-temperature ductility of ZrNb1 and Zircaloy-4. s relative displacement

trix to deform. The two alloys behaved differently in this respect, too. Zircaloy showed residues of a well-developed deformation fracture, which occurred together with areas of brittle failures (Fig. 3, left part). The higher the share of areas with dimple formation, the higher was the deformation before break. A mixed fracture of this type was not obtained for ZrNb 1. Here the ductile dimple fracture sharply changed to brittle failure, generally plate-shaped; generally a faint formation of flat dimples could be noticed (Fig. 3, right part).
Causes for embrittlement in the $\alpha'$ matrix are

- formation of the $\alpha'$ structure after cooling from oxidation temperature,
- hydride formation by hydrogen absorption,
- oxygen uptake.

The morphology of the $\alpha'$ structure depends in a complex way on annealing temperature, cooling rate, and oxygen concentration. The $\alpha'$ structure causes reduced ductility but not complete embrittlement. Samples which were annealed in the $\beta$ area under vacuum thus showed a partially plastic behaviour.

The relations between hydrogen absorption and reduced ductility were particularly investigated in Japan [6–8]. The hydrogen concentration can be considerably increased by oxidation in steam. In the author's investigations, lower hydrogen concentrations (below or within the 100 ppm range) were found for Zircaloy, whereas ZrNb 1 showed low hydrogen uptake only if firmly adherent and crackless oxide layers were
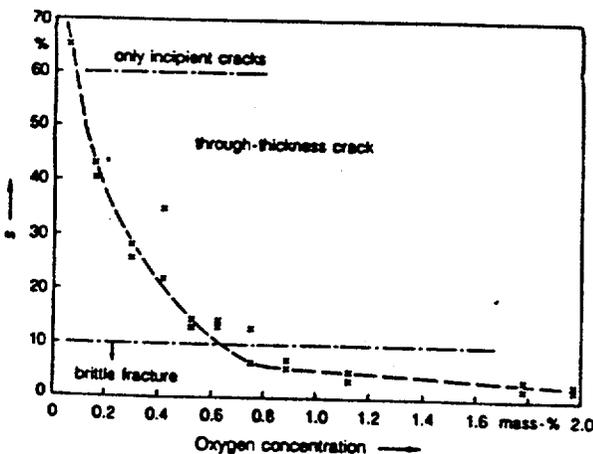
formed. Otherwise there was high hydrogen absorption, with a maximum at 2000 ppm.

The results of ring compression tests are plotted in Fig. 4 in order to check the correlation between hydrogen concentration and ductility at room temperature. Deformations of samples hydrogenated at 400 °C are also shown in this Figure. Although a relation between ductility and hydrogen concentration can be recognized, the test results cannot be unambiguously interpreted on the basis of this parameter.

The effect of oxygen concentration on the ductility was determined for preoxidized and homogenized samples. As is shown in Fig. 5, the ductility decreases with increased oxygen concentration. Fracture occurs, without macroscopically plastic deformation, in the 0.7 per cent range.

It is known from investigations with Zircaloy that the microhardness increases with increasing oxygen concentration [15]. The same can be shown to be true for ZrNb 1. Thus a correlation between microhardness and ductility at room temperature can be expected. Indeed, Fig. 6 shows such a correlation, which does not essentially differ for Zircaloy and ZrNb 1 when samples with high hydride concentrations are disregarded.
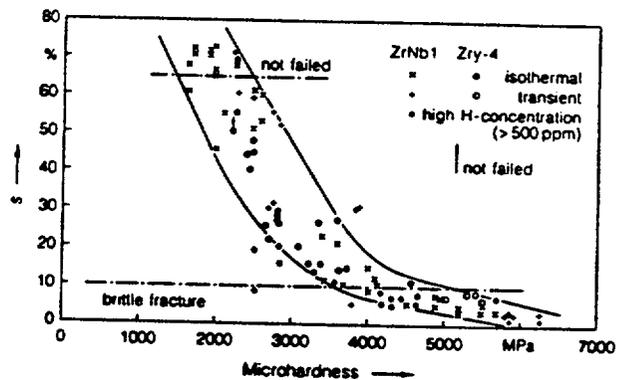


Fig. 6. Dependence of room-temperature ductility on microhardness after high-temperature steam oxidation. s relative displacement

Measurements of the microhardness of ZrNb 1 in the $\alpha'$ matrix after oxidation at and above 1000 °C resulted in higher and more homogeneously distributed values, whereas Zircaloy showed a well-developed heterogeneity in the radial profile of the microhardness. Areas of high micro hardness can be metallographically be identified as $\alpha$ inclusions in the microstructure.

## 4 Discussion

ZrNb 1 is considerably more susceptible to embrittlement than Zircaloy. This is caused, apart from higher hydrogen absorption in ZrNb 1 between 950 and 1000 °C, by higher oxygen absorption and more homogeneous distribution of oxygen in the matrix of ZrNb 1, as can be concluded from microhardness measurements. Three facts are predominantly responsible for this behaviour.

1. ZrNb 1 prematurely forms laterally structurized oxide layers. The thickness of the essentially intact inner oxide layer is rate-controlling. Radial cracks in the outer (white) oxide layer enable direct access of steam. The real oxidation process takes place on the tangential boundary layer of the inner oxide and under conditions of steam Starvation and high hydrogen concentration in the steam. The result is a higher hydrogen absorption. This corresponds to the in-



Fig. 5. Effect of oxygen concentration on room-temperature ductility of ZrNb 1. s relative displacement

fluence of steam supply on the oxidation behaviour of Zircaloy as reported in Refs. [6, 8, 16].

2. The ternary system Zr-Nb-O tends to decomposition where Nb is enriched in the β phase and oxygen is enriched in the α phase. Thus an irregular, only roughly structurized boundary layer is formed, which generates tracks with high diffusion rate (grain boundary, β phase). In this way oxygen can be quickly absorbed in the basic structure. In contrast, a flat growth front with a sharp concentration change, acting as a diffusion barrier, is formed in Zircaloy.

3. The dependence of the free enthalpy on oxygen concentration is different for the systems ZrNb1-O and Zircaloy-O. Thus there is a retransformation of the β phase into the α phase without diffusion during cooling of ZrNb1, whereas Zircaloy shows diffusion-controlled decomposition during cooling. Zircaloy therefore forms α inclusions with high oxygen concentration and α′ areas with low oxygen concentrations. The latter areas, in accordance with fractographic findings, act as ductile zones which can stop cracks and thus ensure partial macroscopic plasticity. A given integral oxygen concentration will therefore be less critical for Zircaloy than for ZrNb1.

## 5 Evaluation of the equivalent oxide-layer thickness criterion

An acceptable range of oxidation is defined by the criterion of equivalent oxide-layer thickness, but an acceptable loss of ductility is actually meant. The correlation between oxidation kinetics and embrittlement is specific for each alloy. It can therefore be expected that the criterion describes facts correctly only when it is used for the alloy for which it was established or for an alloy with similar characteristics as regards oxidation and ductility. According to the results presented in this paper, similar oxidation and ductility characteristics cannot be assumed for ZrNb1 and Zircaloy.

However, the procedure used for these investigations is only an indirect method for safety assurance. Although there are relations between the behaviour during ring compression test, during thermoshock treatment, and during unloading and transport manipulations, these types of behaviour are not completely equivalent. Therefore it cannot be definitely concluded that the 17 per cent criterion must be declined in the case of ZrNb1.

There remains the question whether the criterion is appropriate for providing sufficient safety at a loss-of-coolant accident. Attempts to replace the criterion by more sophisticated algorithms are reported in Refs. [9–13]; obviously the problem has been noticed elsewhere too. Although these attempts enable toughness or thermoshock behaviour to be described more precisely, they still refer to alloy-specific material properties. Moreover, they are more difficult in handling and thus more difficult to verify.

A fundamentally new approach is obviously required. The criterion of equivalent oxide-layer thickness was developed when simulation of the temperature-time response of fuel elements under conditions of insufficient core cooling had become a possibility. Material properties were then not taken into account, or considered only in a very limited approximation. Meanwhile, qualified computer programs have been developed and verified which are able to describe material

properties. It is therefore recommended to revise the criterion in such a way that the fundamental safety-related parameters are directly introduced, i.e., that limits for material properties are defined which ensure that the fuel elements withstand the stress during core flooding and unloading and transport manipulations. This is a task of structural mechanics analysis.

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