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Ambient and high temperature mechanical properties of ZrNb1 cladding with different oxygen and hydrogen content

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ABSTRACT

Zirconium-niobium1% alloy is of remarkable technological importance in VVER reactor applications such as fuel cladding. The low and high temperature mechanical properties of ZrNb1 alloy have significant effect on the behaviour of fuel rods under normal, off-normal and transient operation as well as in accident conditions.

Different thermo-mechanical tests and studies have been performed in KFKI Atomic Energy Research Institute for the better understanding of the behaviour of the oxidised ZrNb1 cladding containing different hydrogen content. Tensile properties of ZrNb1 cladding for different steam oxidised states up to 20 % oxidation level were determined in the temperature range 20 to 300 °C. Radial crushing tests were performed to investigate the process of embrittlement of ZrNb1 and Zircaloy-4 claddings as a function of oxygen and hydrogen content. In an other series of measurements burst tests were carried out in the temperature range 700 to 1200 °C for ZrNb1 samples steam oxidised up to 5% oxidation level.

In the paper the consistency of results with other measurements is presented.

Introduction

Several questions of safe and economic operation of power plants require the more and more precise knowledge of fuel behaviour. At the same time the claim of the increase of burn up and power level, as well as the application of the load-follow operation demand sophisticated computer codes based on extensive experimental background for the prediction of fuel behaviour under in-reactor operation.

Mechanical properties of cladding material are important influencing factors controlling fuel behaviour under normal, off-normal and accident conditions. Despite the considerable scientific and engineering interest on the VVER specific cladding material zirconium-niobium1% (ZrNb1) a limited and somewhat inconsistent information is available for its ambient and high temperature mechanical properties in normal state and at different oxygen and hydrogen content.

The aim of the present work is to determine the ambient and high temperature mechanical properties of ZrNb1 and to compare with the analogous properties of Zircaloy. The other aim is to establish connections between the variation of mechanical parameters of ZrNb1 cladding and the temperature as well as their oxygen and/or hydrogen contents to be used in computer codes.

Experimental methods

Because of the tube geometry of the cladding the importance of main load directions (axial, radial, and tangential) is different in different technological (normal, accident) conditions. The tensile properties at 20-350 °C characterise the fuel behaviour in normal and off- normal operation and under dry storage conditions. The process of embrittlement caused by hydrogen and/or oxygen content can be followed by the results of radial crushing strength and the relative deformation measurements at 20 °C. The measure of ballooning (e.g. in LOCA conditions) can be predicted by means of the results of ultimate hoop stress measurements between 700-1200 °C.

Taking into account the above considerations, tensile tests, radial crushing tests and burst tests were performed at different temperatures on both ZrNb1 and Zircaloy-4 specimens with different hydrogen and oxygen contents.

Samples with different hydrogen and oxygen contents were prepared by

- steam oxidation of samples at different temperatures (900-1200 °C) and oxidation periods (60-10000 s) [1, 2, 3],
- $Ar+O_2$ oxidation of samples at 800 °C with various oxidation periods (700- 11220 s) [4],
- gaseous hydridization of samples at 900 °C [4],
- gaseous hydridization of pre-oxidised samples at 900 °C [4].

The oxygen content of the cladding is uniformly characterised by the equivalent oxidation which is defined as a ratio of the mass gain due to oxygen uptake and the quantity of oxygen needed for the total oxidation of the given Zr alloy sample as stochiometric ZrO_2. In the range of equivalent oxidation 0-27 %, the oxidation level defined in safety criteria for postulated accidents [5] can be obtained by multiplying the value of equivalent oxidation with a geometry dependent factor (0.96 for the Zircaloy and 0.94 for the ZrNb1 tubes, respectively). The thickness of the ZrO_2 layer on the surface of tubes can be estimated as 10 μm per 1 % equivalent oxidation in this range of oxidation.

The hydrogen content of the cladding was determined (uniformly in mass ppm) either by hydrogen extraction from samples in solid state using nitrogen as a carrier gas and thermal conductivity cell as detector [6] or by the quantity of the absorbed gas [4]. In the case of steam oxidation, the hydrogen content was not always directly measured. For these cases the hydrogen content was estimated on the basis of a pre-determined relationship between hydrogen content and equivalent oxidation (Figure 1.). The curve corresponding to Zircaloy-4 cladding based on the results of Leistikow and G. Schanz [7] is also depicted on Figure 1.

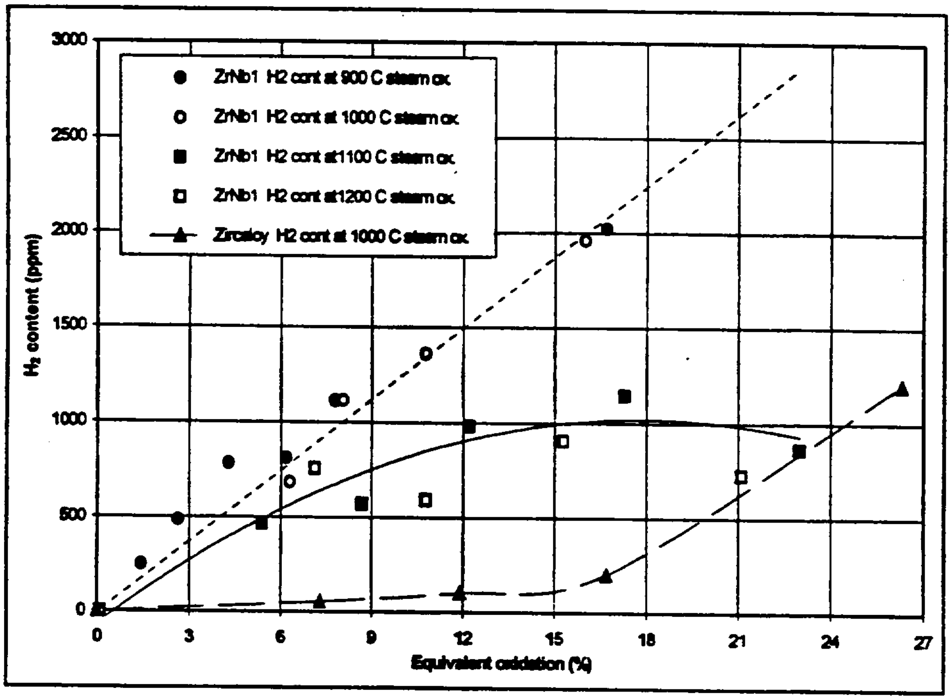

Figure 1.
Hydrogen content as a function of equivalent oxidation in steam oxidation

Results of measurements

The mechanical behaviour of unoxidised and hydrogen free samples and samples of different hydrogen and oxygen content were investigated with different methods. Extensive studies of the changes of direction dependent mechanical parameters as a function of temperature and the oxygen and/or hydrogen content were performed.

Tensile tests

Standard tensile tests were carried out at ambient temperature on "as received" and differently heat treated samples. The results showed that the stress relieving treatment at 700 °C did not cause significant changes in the mechanical parameters. The standard error of ultimate tensile stress (UTS), yield stress and elongation were 2.6, 9.8 and 7.1 % respectively [8]. Therefore the as received samples can be considered as being close to the equilibrium state.

The results are summarised in Table 1. The ultimate tensile stress and yield stress results agree with the values measured by J. Vesely and co-workers [9]. The results of tensile tests performed on tube specimens at 20 °C gave good agreement in the values of ultimate tensile strength with the corresponding results measured by using standard specimens. At the same time the values of elongation differed with a factor of two in the two measurements. The higher values of elongation measured with tube geometry are in accordance with the data of Russian data base [10]. The Russian tube measurements were performed with cold worked specimens which explains the deviation of results.

Comparing the tensile parameters of ZrNb1 to those of Zircaloy-4 one can see the better mechanical properties of Zircaloy-4. This is also illustrated in Table 1.

Table 1.
Mechanical parameters of ZrNb1 and Zircaloy-4

Sources Form of sample	**UTS [MPa]**		**Yield stress [MPa]**		**Elongation [%]**		**Ref.**
	Stand.	tube	Stand.	tube	Stand.	tube	
Present work	417	370	234	-	24	53	
Czech work	407		223		39		[9]
Russian data base	380	410	210	240	30	48	[10]
Australian work	390		322		50		[11]
Zircaloy-4	*720*		*550*		*21*		[9]

The results of measurements for oxidised samples are shown in Table 2 and on Figure 2. In the first series of measurements [2] the samples were oxidised in steam, while some other samples were oxidised in air. Data from the Russian data base [10] are also plotted on Figure 2.

Table 2.
Mechanical properties of ZrNb1 cladding at temperature as a function of equivalent oxidation

Equivalent oxidation [%]	thickness of layer $_{ZrO2}$ [mm]	Estimated H_2 content [ppm]	at 20 °C		at 150 °C		at 300 °C	
			UTS [MPa]	Elongation [%]	UTS [MPa]	Elongation [%]	UTS [MPa]	Elongation [%]
0.0	0.0	0	361	53.1	277	60.8	240	61.5
0.0	0.0	0	372	53.4				
1.0	9.5	300	461	29.1				
1.1	11.1	300	463	25.2	359	33.1	275	38.8
1.5	14.8	350			349	22.7		
2.1	20.8	400	507	15.0				
2.1	21.0	400	495					
2.5	25.3	450			380	14.1	270	14.6
3.2	22.8	500			401	13.2		
4.0	40.4	600	351					
4.2	41.6	600	298		393	12.5		
5.6	54.4	750	236					
7.1	69.2	1050	176		139			
10.4	104.3	1350	81					
19.9	197.8	2400	14					
**17.9*	*174*	*0*	*391*	*8.1*				
**20.5*	*200*	*0*	*380*	*8.2*				
**51.9*	*520*	*0*	*294*	*5.5*				

Remark: "*" Air oxidation [8]

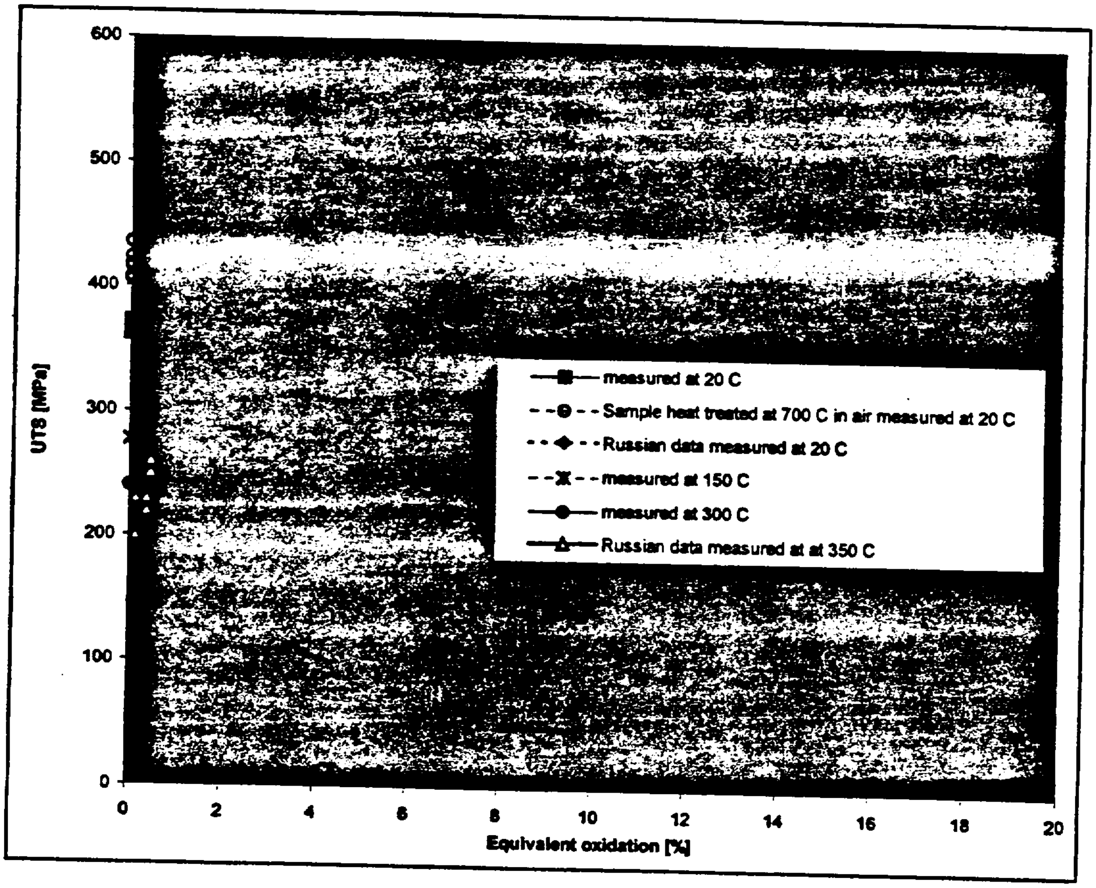

Figure 2.
High temperature UTS of ZrNb1 cladding as a function of oxygen content

From the results of tensile tests of air oxidised samples one can see that UTS does not depend on the equivalent oxidation. This can be explained only by the absence of hydrogen, since for samples oxidised in steam containing considerable quantity of hydrogen the UTS seems to be strongly dependent on the equivalent oxidation.

In the case of steam oxidised samples with relatively low (up to 400 ppm) hydrogen content the ultimate tensile stress of ZrNb1 cladding at different temperatures (20-300 °C) up to 2-3 % equivalent oxidation increases with increasing oxygen content, then drastically decreases (Figure 2. and Table 2.) probably due to the higher hydrogen content. The elongation monotonously decreases with increasing oxygen content, above about 400-500 ppm hydrogen content the elongation cannot be measured because of the embrittlement.

One can conclude that the hydrogen content is responsible for the degradation of mechanical properties much rather than the oxidisation. This suggestion seems to be justified by the results of further mechanical investigations.

Radial crushing tests

The results of the radial crushing tests well indicate the embrittlement of the cladding materials due to the oxidisation and/or hydridization process.

The greater stiffness of Zircaloy-4 appears in the values of radial crushing strength, (R_{mk}) too. The values of radial crushing strength of ZrNb1 cladding were orderly lower with a factor of 0.75-0.80 than that of Zircaloy-4 cladding of the same state (Table 3., 4. and Figure 3 a, b,).

Table 3.
Radial crushing strength (R_{mk}) and relative deformation of ZrNb1 cladding with different hydrogen content as a function of equivalent oxidation

Equiv. oxid. [%]	**R_{mk} [MPa]**							
	H_2=0 ppm	H_2=30 ppm	H_2=100 ppm	H_2=300 ppm	H_2=700 ppm	H_2=1000 ppm	H_2=3000 ppm	H_2=9000 ppm
0.00	t. pd.	t. pd.	t. pd.	2444	1352	1100	850	950
1.34	t. pd.	t. pd.	932	888	1028	730	480	450
2.87	t. pd.	t. pd.	1126	1219	1316	60	60	60
4.30	t. pd.	t. pd.		1235	1291			
5.13	t. pd.	t. pd.	945	939	1235			
5.40				939	1235			
6.30					751			
7.14					634			
8.70				575		645		
10.80						563		
12.20						371		
15.30						399		
17.30						300		
21.10					305			
23.00					258			
	Relative deformation [%]							
0.00	t. pd.	t. pd.	t. pd.	69.0	54.2	22.0	3.5	2.5
1.34	t. pd.	t. pd.	39.8	9.9	6.6	3.6	2.2	2.2
2.87	t. pd.	t. pd.	35.2	12.1	9.9	1.0	0.5	0.5
4.30	t. pd.	t. pd.		12.0	8.1			
5.13	t. pd.	t. pd.	32.8					
5.40				5.5	9.8			
6.30					5.7			
7.14					5.2			
8.70				4.4		6.5		
10.80						6.9		
12.20						4.1		
15.30						4.3		
17.30						3.7		
21.10					2.5			
23.00					3.3			

"t. pd" means total plastic deformation

Table 4.

Radial crushing strength (R_{mk}) and relative deformation of Zircaloy cladding with different hydrogen content as a function of equivalent oxidation

Equiv. oxid. [%]	**Relative deformation [%]**					**R_{mk} [MPa]**				
	H_2=0 ppm	H_2=30 ppm	H_2=100 ppm	H_2=300 ppm	H_2=700 ppm	H_2=0 ppm	H_2=30 ppm	H_2=100 ppm	H_2=300 ppm	H_2=700 ppm
0.00	t. pd.	73.6	66.1	59.6	52.0	t. pd.	3383	2658	2537	2276
1.07			17.6					1406		
1.35	70.6	35.3		10.2	9.1	3150	1648		1406	1577
1.61		40.0	16.2				1695	1406		
2.18	65.0			7.4	12.6	2617			1385	1531
3.78			15.4					1410		
4.18	55.4			10.2	10.2	2072			1268	1560
4.54		23.7					1407			
7.35		19.3					1340			
11.80		13.2					1100			
16.70			15.9					590		
26.30					7.1					245

"t. pd" means total plastic deformation

The radial crushing strength of ZrNb1 cladding with up to 700 ppm hydrogen is significantly increasing up to about 5 % equivalent oxidation, then it is decreasing. In samples of higher than 700 ppm hydrogen content the improving effect of oxygen cannot be seen. This effect of oxygen cannot be detected at all in the case of Zircaloy-4 (Figure 3. a, b)

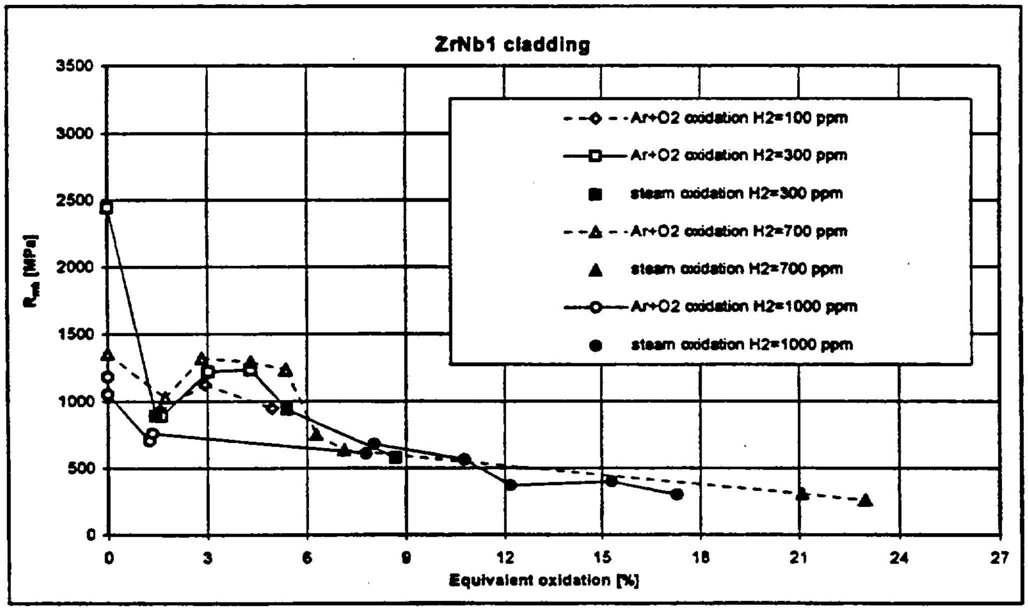

Figure 3. a.

Radial crushing strength (R_{mk}) of ZrNb1 cladding with different hydrogen content as a function of equivalent oxidation

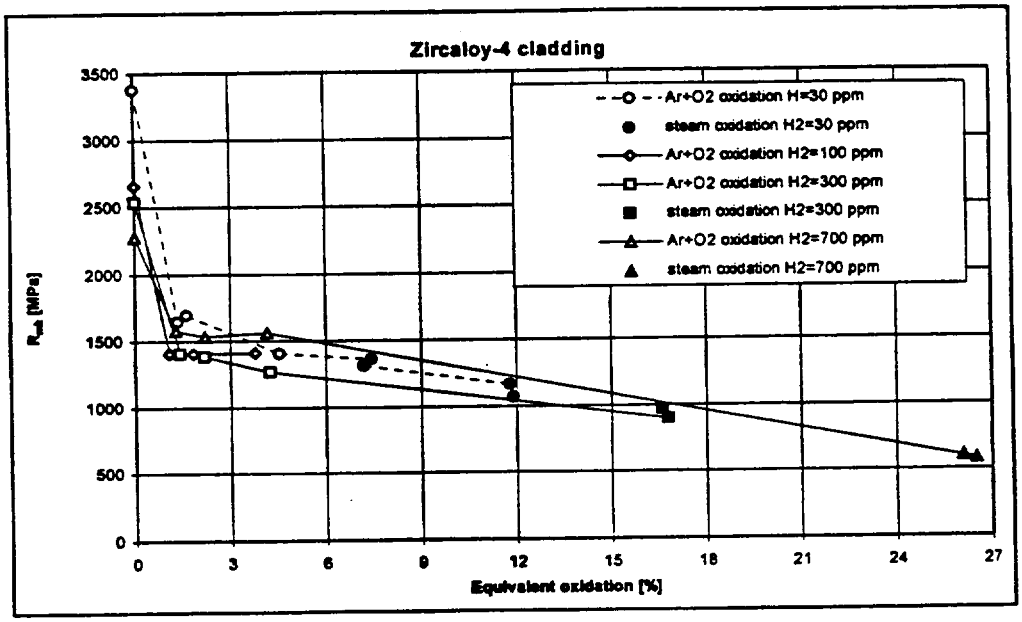

Figure 3. b.
Radial crushing strength (R_{mk}) of Zircaloy cladding with different hydrogen content as a function of equivalent oxidation

The process of embrittlement due to the hydrogen and/or oxidisation can be followed by the relative deformation of the samples measured at the first break. The bigger the embrittlement the smaller is the deformation up to break. Above 1% equivalent oxidation the process of embrittlement begins at 30 ppm hydrogen content in the case of Zircaloy-4, while in the case of ZrNb1 this process starts at only 100 ppm hydrogen (Figure 4 a, b).

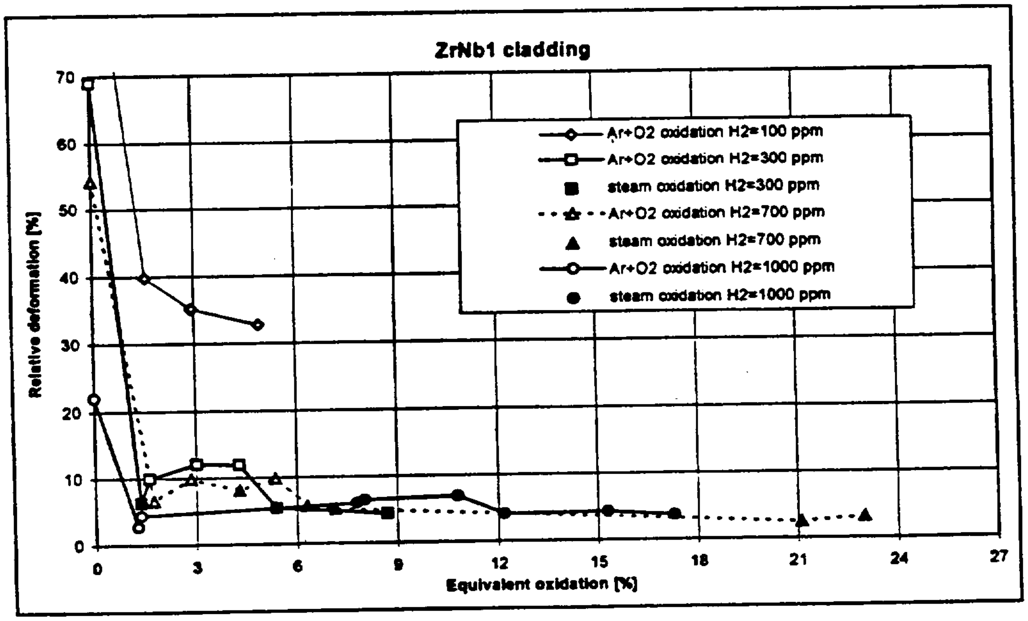

Figure 4. a.
Relative deformation of ZrNb1 cladding with different hydrogen content as a function of equivalent oxidation

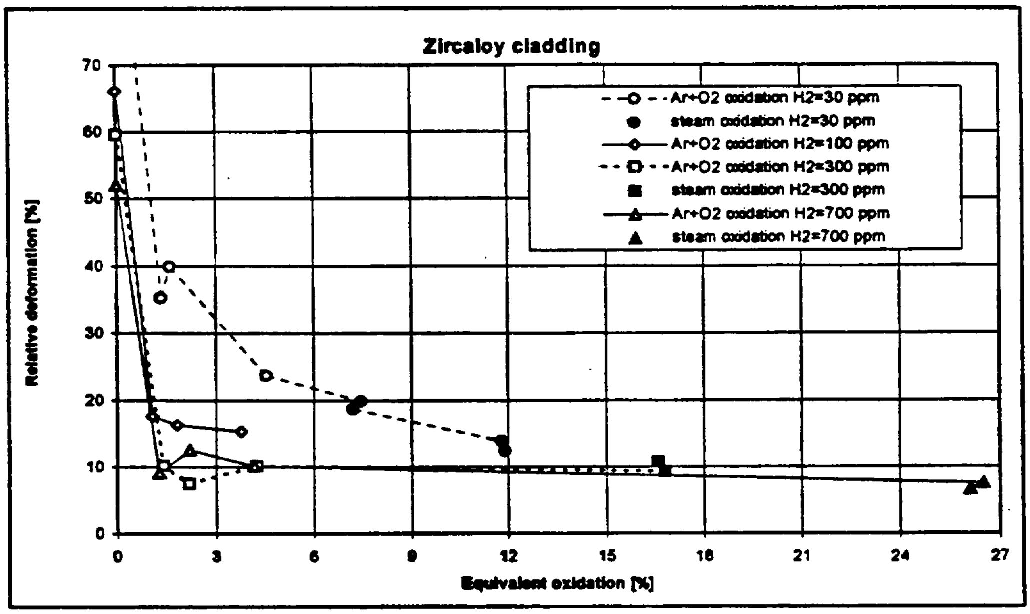

Figure 4. b.
Relative deformation of Zircaloy cladding with different hydrogen content as a function of equivalent oxidation

The ZrNb1 samples remain totally plastic below 100 ppm hydrogen. Above 700 ppm hydrogen content the embrittlement becomes complete for both claddings independently of the oxidisation.

Burst tests

From the results of burst tests carried out with ZrNb1 and Zircaloy claddings in the temperature range of 700-1200 °C the dependence of maximum hoop stress on the temperature is presented on Figure 5 (unoxidised samples). From this figure the better mechanical properties of Zircaloy-4 can be seen again.

For the two types of claddings the maximum hoop stress values measured at different temperatures between 700-1200 °C were extrapolated to 20 and 350 °C. They show very good agreement with the results of J. Vesely and co-workers [9]. Using also the data of J. Vesely and co-workers a second order equation can be given for the dependence of hoop stress on the temperature in the range of 20-1200 °C.

The variation of hoop stress of ZrNb1% cladding as a function of the equivalent oxidation can be seen in Table 5. and Figure 6. (oxidised samples).

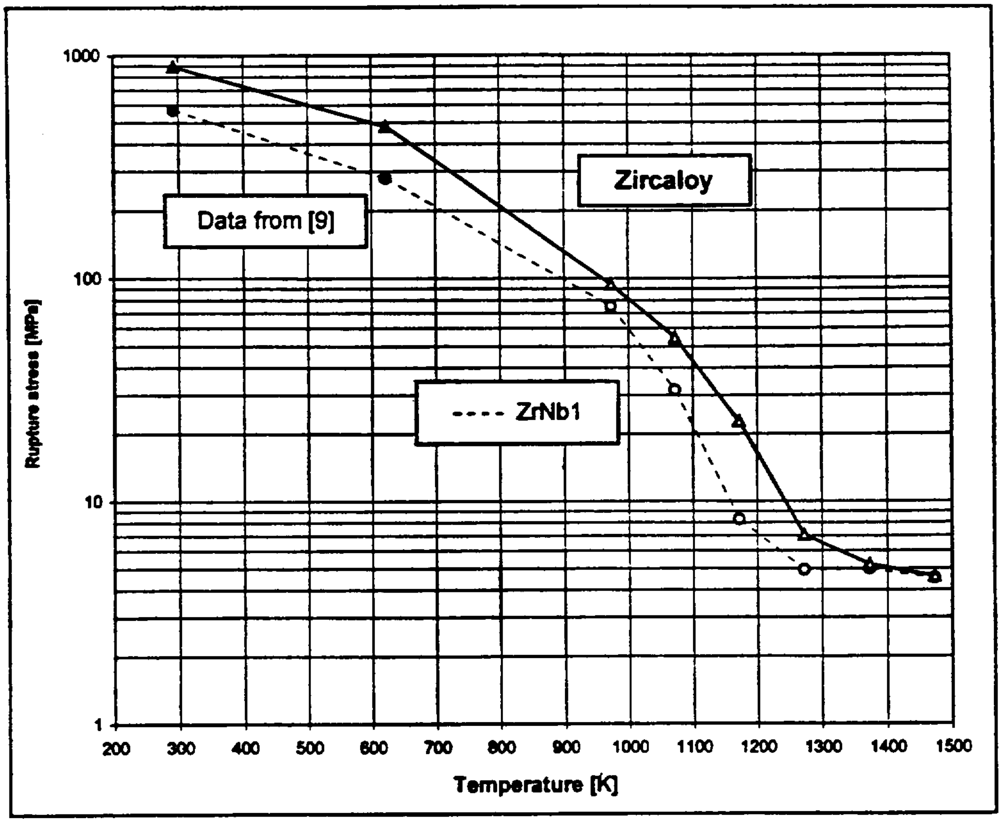

Figure 5.
Temperature dependence of the hoop stress of ZrNb1 and Zircaloy-4 claddings

Table 5
Rupture stress of ZrNb1 cladding as a function of equivalent oxidation

Equiv. ox. %	ZrO_2 layer μμ	Estm. H_2 ppm	Rupture stress [MPa]					
			700 °C	800 °C	900 °C	1000 °C	1100 °C	1200 °C
0.0	0	0	75.3	31.7	8.3	4.9	5.0	4.5
0.7	6	<100	90.0	49.3	14.7	8.8	6.2	
1.4	12	200	93.0	52.4	14.8	7.6		
2.0	16	300	90.8	54.3	14.9			
2.3	19	300	97.1		19.1	10.9	6.7	5.5
2.9	24	420		36.4				
4.2	35	560	50.7					
5.7	49	750	59.5					

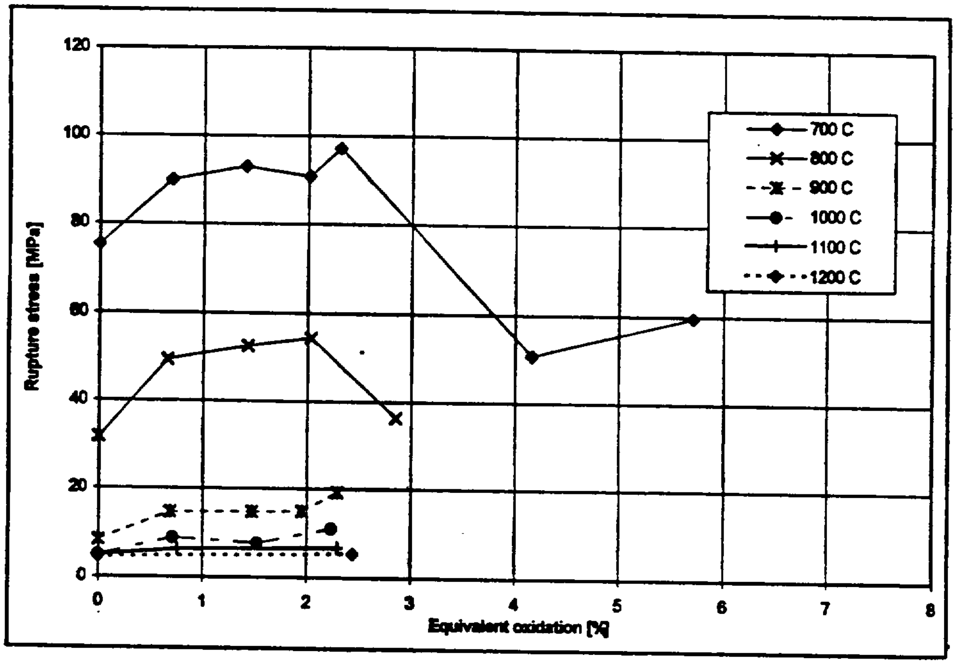

Figure 6.
The hoop stress of ZrNb1% claddings as a function of equivalent oxidation

As a function of equivalent oxidation the hoop stress at break increases up to 2-3% and then it decreases, while the average deformation continuously decreases [12] similarly as in the case of tensile and crushing tests. In the burst tests the effect of oxygen can be well distinguished from those of hydrogen, since the hydrogen content of samples hardly exceeded 500-600 ppm.

Conclusions

A coherent picture on the mechanical parameters of ZrNb1% cladding material was reached for normal and oxidised/hydridised states. The tendencies found for the three load directions are similar to each other. The measurements performed at the KFKI Atomic Energy Research Institute show a good agreement with the results known from the literature.

It seems to be reasonable to explain the variation of mechanical parameters of ZrNb1 cladding by the hydrogen uptake rather than by the oxygen content.

Though the basic mechanical properties of Zircaloy are more advantageous compared to those of ZrNb1%, the embrittlement caused by hydrogen starts in Zircaloy-4 at lower hydrogen content than in ZrNb1%. At the same time in the ZrNb1% cladding at lower than 400-500 ppm hydrogen content the oxidation improves the mechanical parameters up to 2-5% equivalent oxidation.

References

1. J. Frecska, G. Konczos, L. Maróti and L. Matus.: Oxidation and Hydriding of ZrNb1% Alloys by Steam KFKI-1995 -17/G report

2. Á. Griger, L. Maróti and L. Matus.: Behaviour of VVER type fuels under normal off-normal and accident conditions (1998) KFKI report (in Hungarian)

3. L. Maróti, L. Matus and P. Windberg.: Fuel Behaviour: Ballooning of clad under LOCA condition, experiments and results (1995) KFKI report (in Hungarian)

4. L. Matus and L. Vasáros: Mechanical properties: Embrittlement caused by hydrogen uptake (1998) KFKI report (in Hungarian)

5. Compendium of ECCS research for realistic LOCA analysis, NUREG-1230, (R4) US NRC (1988)

6. Á. Griger and E. Kovács-Csetényi: Determination of Hydrogen Content of ZrNb1% (1995) ALUTERV-FKI report

7. S. Leistikow and G. Schanz: The oxidation behaviour of Zircaloy-4 in steam between 600 and 1600 °C (1985) Werkstoffe und Korrosion **36**, 105-116

8. E. Czoboly, L. Maróti and L. Matus: Fuel behaviour (1990) KFKI report

9. J. Vesely, M. Valach, Z. Frejtich and V. Priman: Creep Properties of non-Irradiated ZrNb1 Cladding Tubes under Normal and Abnormal Storage Conditions (1998) to be published

10. IBRAE database: Thermophysical and mechanical properties of Zr-Nb alloys (1999)

11. W. R. Thorpe and I. O. Smith: Tensile Properties of Zr-wt1%Nb Alloy (1978) J. of Nuclear Materials **78**, 49-57

12. Cs. Győry, Z. Hózer, I. Maróti and L. Matus: VVER ballooning experiments (1998) Enlarged Halden Programme Group Meeting on "High Burn-up fuel Performance, Safety and Reliability ....", Lillehammer, Norway 15th -20th March 1998 Vol. II. 1-8, HPR-349