INVESTIGATION OF LOCAL MECHANICAL PROPERTIES OF ZIRCONIUM ALLOYS USING NANOINDENTATION

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1. Introduction

Zirconium alloys are used in nuclear industry, mainly because of their low thermal neutron cross section, for their good mechanical properties and corrosion resistance. These alloys are widely used in production of nuclear fuel cladding tubes serving as the first barrier between the fuel and the surrounding environment. Zirconium shows high affinity to hydrogen, oxygen and nitrogen, forming stable hydrides, oxides, nitrides and interstitial solid solutions. The presence of oxygen and hydrogen has great influence on properties of the microstructure. Oxygen stabilizes the α phase, enlarges the α domain in the phase diagram and causes interstitial solid solution forming. Hydrogen stabilizes the β phase, causes higher solubility of oxygen in Zr at temperatures between 800–1200 °C, influences the redistribution of oxygen and causes the decrease of α – β transformation temperature.

The problem of oxide peeling on pure Zr is solved by the addition of suitable alloying elements Cr, Fe, Ni (stabilizing the β phase), which do not dissolve in the zirconium matrix and form small inclusions of intermetallic phases. Addition of Sn (stabilizing the a phase) reduces the adverse effect of nitrogen. Zirconium alloys were developed in this way, having coherent oxide layer, which do not have tendency to peel. In order to improve mechanical and corrosion properties, other alloy elements can also be added: Al (stabilizing the α phase), Nb, Cu, V and Mo (stabilizing the β phase). High corrosion resistance is attained by softening the structure with soft precipitates of β-Nb on grain boundaries and also in the matrix.

During the fuel cycle in water-cooled reactors, the outer region of the cladding tube is in contact with the cooling medium (water) with the temperature of 320 °C and pressure of 16 MPa. During the operation, oxidation of Zr occurs and hydrogen is released (part of it is absorbed into the alloy). The forming oxide creates a barrier between metal and water and slows corrosion rate. Improvement in physical, mechanical, technological and corrosion properties requires development of new alloys offering longer fuel burn up cycle, a possibility to use higher quality fuel and enhanced safety.

Loss of coolant accident (LOCA) can occur in water-cooled reactors when, due to a broken pipe, water flows out. The loss of moderator occurs within ten seconds or less and the nuclear fission stops immediately. Temperature of the cladding increases to approximately 1000 °C, which results in high temperature oxidation (HTO). The reaction between steam and cladding surface occurs. The reactor emergency system floods the reactor with water in short time and rapidly cools down the cladding tubes.

During the heating period, the structure of the material transforms: the α phase (hcp) changes to the high temperature β phase (bcc). The maximum amount of oxygen, which can be dissolved in the β phase, depends on temperature. The exposure to high temperature atmosphere is accompanied by oxygen and hydrogen uptake. Part of oxygen forms the oxide layer during oxidation and the remaining part dissolves in the metal. The amount of oxygen dissolved in the metal depends on temperature: the higher the temperature, the higher the amount of oxygen dissolved in the metal. Oxygen concentration gradient occurs with higher concentration levels under sample surface.

Due to the rising oxygen content, the β phase transforms back to hcp α-Zr(O), α phase stabilized by oxygen, even at higher temperatures, which is not changed by further cooling. During the cooling period, the remaining β phase transforms to hcp α phase (usually called prior β[1,2]) and β phase stabilizing elements (H, Fe and Cr) diffuse to the non-transformed β phase. Thus the a phase lamellas are formed which are depleted of these elements, despite the fact that the maximal admissible concentration of oxygen in β at higher temperatures is exceeded[1]. Hydrogen causes the precipitation of hydrides during cooling. Faster cooling promotes the formation of ZrH (γ), while the slower one leads to formation of ZrH_{2-x}.

The microstructure of the material after HTO and after the cooling consists of the oxide layer ZrO_2, oxygen stabilized α-Zr(O) and α phase enriched with H, Fe and Cr which create precipitates. The α-Zr(O) layer is very brittle and thus the α phase is the only factor responsible for remaining ductility and toughness of the material. The character of the α-Zr(O) layer depends on the chemical composition of the alloy. Zr-alloys containing Sn (α stabilizer) form uniform layers, whereas in alloys containing Nb (β stabilizer), the layer is non-uniform and acicular[1,2] (see Fig. 1).

2. Experimental

The samples were small tubes with the length of 30 mm and outer diameter of 9 mm and 0.6 mm wall thickness, which are identical to actual cladding tubes. Chemical composition: 1.0–1.1 % Nb, 3 ppm H, 20 ppm N, 100 ppm C, 840 ppm O. The course of LOCA was simulated in laboratory conditions in UJP Praha[2]. Samples were heated at 950 °C, 1000 °C, 1050 °C, 1150 °C and 1200 °C in steam for different time, see Tab. I. After the HTO stage and hardening in water with ice, the tubes were cut to 3 mm-thick rings and then embedded in resin or in conductive substance (for following SEM analyses) and polished. Samples were examined by X-Ray diffractometer equipped with high-temperature chamber[3], scanning electron microscope with EDAX[4] and by Nanoindenter XP.

Table I
Experimental samples and measured mean values

Sample temperature [°C] / time [min]	H_{IT} [GPa]	E_{IT} [GPa]
950 / 0	2.88 ± 0.27	111.1 ± 2.6
950 / 3	2.93 ± 0.16	111.3 ± 4.4
950 / 6	3.21 ± 0.24	106.1 ± 3.0
950 / 9	3.40 ± 0.20	115.3 ± 3.7
950 / 15	3.19 ± 0.17	105.5 ± 2.7
1000 / 9	3.61 ± 0.34	106.7 ± 5.4
1000 / 15	3.69 ± 0.35	110.0 ± 5.3
1050 / 0	3.32 ± 0.25	107.7 ± 4.5
1050 / 3	3.53 ± 0.24	109.1 ± 3.8
1050 / 6	3.63 ± 0.23	110.3 ± 4.3
1050 / 9	3.95 ± 0.24	113.5 ± 3.9
1100 / 3	3.76 ± 0.28	108.9 ± 2.9
1100 / 6	3.98 ± 0.28	113.8 ± 5.1
1100 / 9	4.11 ± 0.24	112.4 ± 3.9
1100 / 15	3.82 ± 0.21	108.7 ± 3.3
1150 / 0	3.14 ± 0.27	111.3 ± 3.8
1150 / 3	3.98 ± 0.22	113.0 ± 3.7
1150 / 9	4.62 ± 0.24	118.8 ± 4.2
1200 / 3	4.67 ± 0.20	116.1 ± 3.0
1200 / 6	4.61 ± 0.38	106.9 ± 1.9
1200 / 9	5.44 ± 0.33	116.4 ± 3.6
1200 / 15	4.98 ± 0.29	106.9 ± 3.0

The instrument enables to perform instrumented indentation where the displacement of indenter and load data are recorded during the loading and unloading periods (*F* – *h:* indentation curve). The indentation hardness H_{IT} and indentation modulus of elasticity E_{IT} were measured by the IIT (Instrumented Indentation Testing) method[5]:

$$H_{IT} = \frac{F_{max}}{A_p}$$

where F_{max} is the maximum load; A_p is the projected contact area of the indent.

$$E_{IT} = \frac{1-(\nu_s)^2}{\frac{1}{E_r} - \frac{1-(\nu_i)^2}{E_i}}$$

where the indices *i* and *s* are related to properties of the indentor or sample material (modulus of elasticity, Poisson ratio) and E_r is reduced modulus of elasticity:

$$E_r = \frac{S \cdot \sqrt{\pi}}{2 . \beta \sqrt{A_p(h_c)}}$$

where *S* denotes contact stiffness (the initial slope of the unloading curve), β is correction constant for the indenter tip shape (for Berkovich indenter: β ≈ 1.034), A_p is the projection of contact area and h_c is contact depth:

$$h_c = h - \varepsilon \frac{P_{max}}{S}$$

where ε is constant dependent on the indenter geometry[6].

Nanoindentation measurements were performed with the Berkovich indenter with the load of 8 mN. The indents were made in three parallel rows with the starting point at the oxide – metal interface and the distance of 5 µm between each other. They were documented by using an optical microscope or a SEM. The min – max intervals were recorded (Fig. 1), with the assumption that they correspond with the α phase properties, then mean values were calculated.

Calculated values of indentation hardness and modulus of elasticity of the α (prior β) phase are shown in Tab. I. and Fig. 2 and 3.

The indentation hardness generally increases with the temperature of exposure. It depends on higher oxygen content[4]. The indentation modulus of elasticity is nearly constant: 111.4 GPa ± 4.2 GPa (standard deviation is approximately 4 % from mean value).

Ratio of measured values of indentation modulus of elasticity E_{IT} and indentation hardness H_{IT} (ref.[7]) is shown

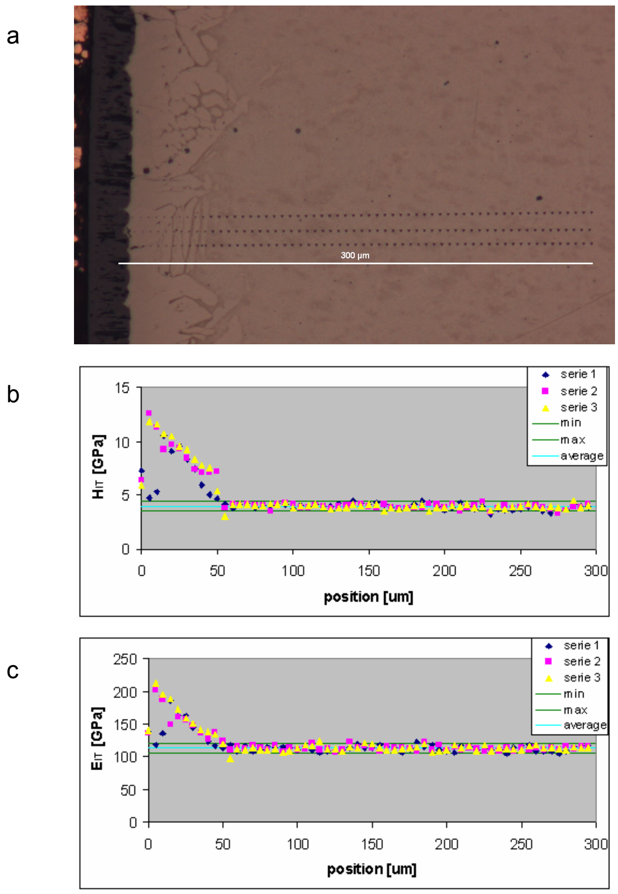

Fig. 1. **a) Micrograph of sample with exposition temperature 1050 °C and time 9 min, b) measured value of indentation hardness, c) measured value of indentation modulus of elasticity**

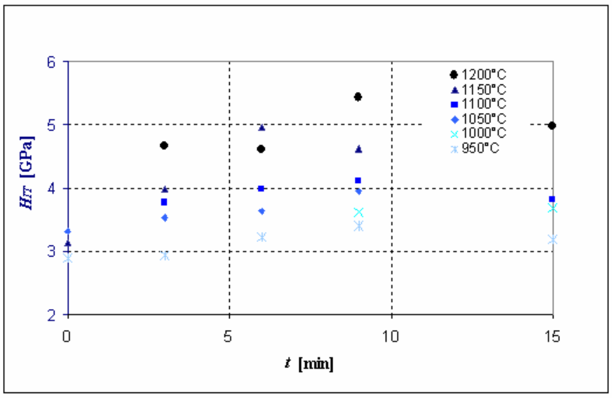

Fig. 2. **Indentation hardness of samples with different exposition temperature *vs.* exposition time**

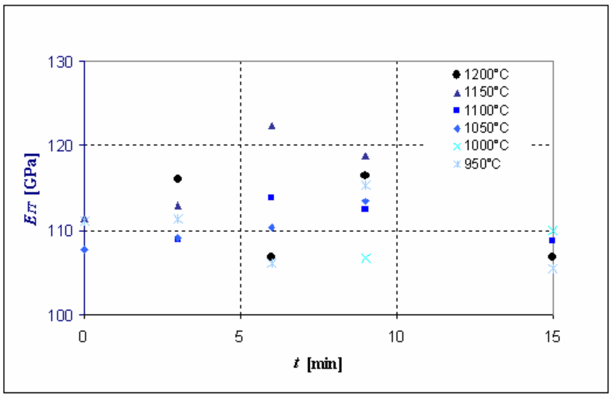

Fig. 3. **Indentation modulus of elasticity of samples with different exposition temperature *vs.* exposition time**

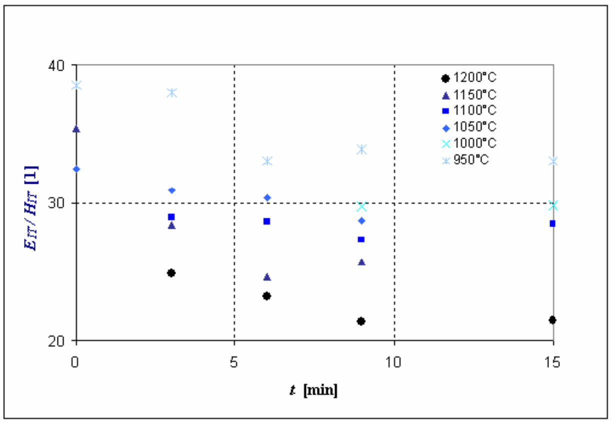

Fig. 4. **Ratio of measured values of indentation modulus of elasticity E_{IT} and indentation hardness H_{IT} *vs.* exposition time**

in Fig. 4. This ratio mostly decreases with the temperature of exposure.

Samples were measured at UJP Praha by the pressure testing method at 135 °C and ductility was determined[2]. Samples are brittle when their hardness is more than 4 GPa (see Fig. 5).

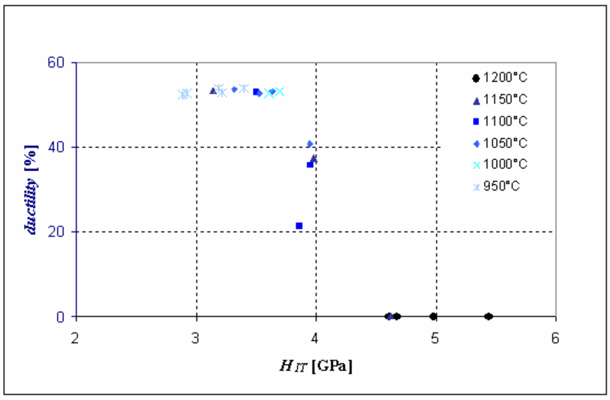

Fig. 5. **The ductility *vs.* indentation hardness of samples with different exposition temperature**

3. Conclusion

This paper is based on long-time investigation and characterization of mechanical and related properties of a new Zr1Nb alloy. The samples were analysed using nanoindentation method.

The indentation hardness of the α (prior β) phase was determined and it was found out that indentation hardness increases with the temperature of exposure. On the contrary, the indentation modulus of elasticity is nearly constant so that ratio indentation hardness and indentation modulus decreases with the temperature of exposure.

The indentation hardness correlates with ductility measured by the pressure testing method.

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O. Bláhová *(New Technology Research Centre, University of West Bohemia, Plzeň):* **Investigation of Local Mechanical Properties of Zirconium Alloys Using Nanoindentation**

Samples from Zr1Nb alloy were tempered after various temperatures and various times prior to hardening. This process simulated the LOCA (Loss Of Coolant Accident) conditions when, due to a broken pipe, water flows out. The loss of moderator occurs and temperature of the cladding increases, which results in high temperature oxidation. The emergency system floods the reactor with water in short time and rapidly cools down the cladding tubes.

This paper presents the evaluation of local mechanical properties on samples after this simulation process. The indentation hardness and indentation modulus of elasticity were evaluated by nanoindentation method.