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Influence of hydrogen content on the strength and the presence of defects in ε-zirconium hydride

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Abstract

The change in the bending strength of ε-zirconium hydride samples with compositions $ZrH_{1.82}$–$ZrH_{1.98}$ was investigated. The structure and presence of defects in hydrides of these compositions were studied using optical microscopy and mercury porosimetry methods. It was shown that the non-monotonous decrease of the strength of zirconium hydride with changing composition from $ZrH_{1.82}$ to $ZrH_{1.98}$ is caused by an increase in the number of defects in the material during saturation by hydrogen. The main defects influencing the hydride strength are micro-cracks caused by elements of the twinning structure.

Keywords: Zirconium hydride; Strength; Structure; Micro-cracks

1. Introduction

It has been shown that the bending and compression strength of ε-zirconium hydride decreases monotonously with increasing hydrogen content [1–3]. Together with this feature, non-monotonous concentration changes of the elasticity module, micro-brittleness and K_{1C} parameter have been reported [4,5], and extreme values for these characteristics were reported for compositions $ZrH_{1.90}$–$ZrH_{1.94}$. These different changes in the properties of ε-zirconium hydride with increasing hydrogen content are probably caused by material structural features, in particular by defects.

The objective of this work was to study the bending strength change (σ_b) and zirconium hydride structure in the range of compositions $ZrH_{1.82}$–$ZrH_{1.98.}$

2. Experimental

Compact hydride samples were prepared by the saturation of zirconium metal of various purities by hydrogen at high temperature and then slow cooling under equilibrium (for each desirable hydride composition) gas pressure. Remelted zirconium iodide containing Zr≥99.9, $C \leq 2\times10^{-2}$, N, $S \leq 4\times10^{-3}$, $Nb \leq 10^{-2}$ and $Fe \leq 10^{-2}$ (mass%), as well as technical zirconium with an increased niobium content (~1.2 mass%) and oxygen (~0.06 mass%), were

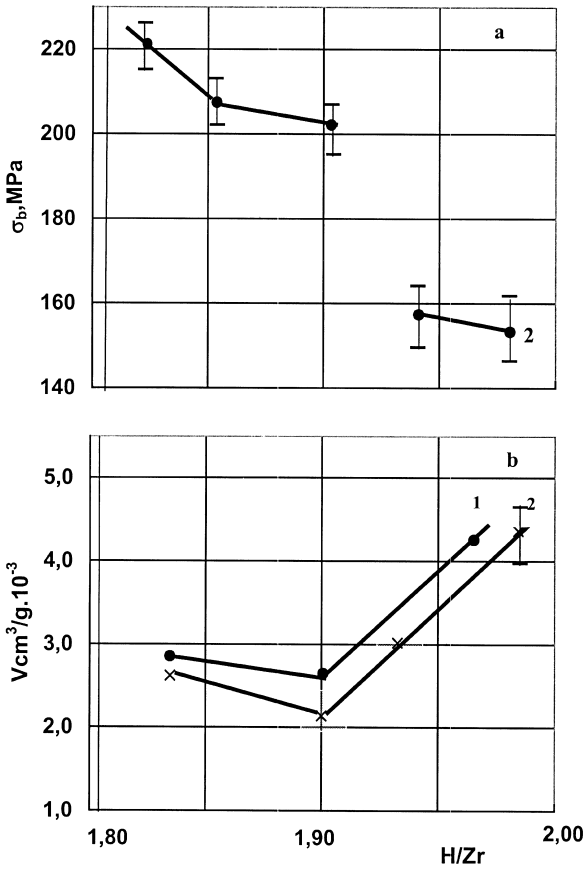

Fig. 1. Change of bending strength (a) and specific void volume (b) of ε-zirconium hydride vs. hydrogen content. Samples with grain size (μm): 1, 3000–5000; 2, 40–80.

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utilized. This allowed us to obtain samples with identical hydrogen content, but with different grain sizes, 3000–5000 and 40–80 μm, respectively. Coarse grain hydride was used for structural investigations, and fine grain hydride for strength measurements. The hydrogen content of the samples was determined by chemical methods with an accuracy of 0.01 mass%.

Three-point (base 30 mm) bend tests were conducted using prismatic-shaped zirconium hydride samples (3×3×35 mm) at 20°C on a 1958-Y10 test machine. The deformation rate was 1 mm/min. The root-mean-square measurement error of σ_b was <14 MPa.

The hydride structure was examined on micro-sections by optical microscopy; the surfaces were exposed to

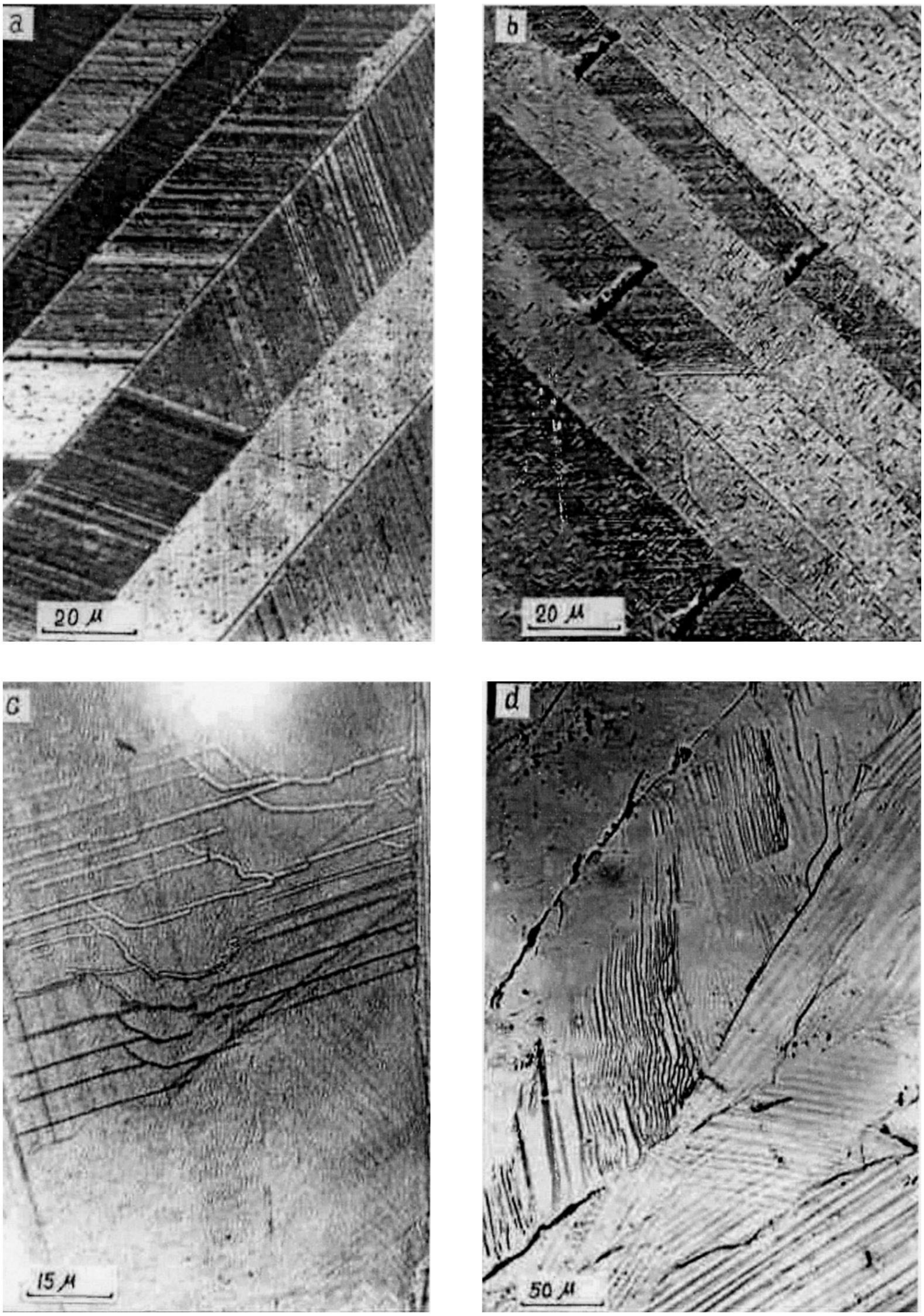

Fig. 2. Change of structure and presence of defects in ε-zirconium hydride vs. hydrogen content. (a) Twin structure, $ZrH_{1.90}$; ×800. (b) Re-orientation and micro-cracks in twins, $ZrH_{1.95}$; ×800. (c) Nucleation of channels–voids, $ZrH_{1.95}$; ×1000. (d) Packets of channels–voids in a grain, $ZrH_{1.98}$; ×300.

chemical polishing in a hot water solution of HF and HNO_3 acids with removal of material to 200 μm depth.

The open pore specific volume of hydride samples of various composition was determined by the mercury method using a P-3M porosimeter on powder samples (particles 2–4 mm in size, sample weight 3 g).

The equivalent radius of the measured voids was in the range from 0.003 to 30 μm; the measurement error of the void volume was 0.006 cm^3/g.

3. Results and discussion

The dependence of the bending strength (σ_b) on the hydrogen content is presented in Fig. 1a, and the results of measurements of the specific void volume in hydride samples of various composition are presented in Fig. 1b. It can be seen from Fig. 1a that the value of the bending strength changes non-monotonously from 220 to 150 MPa, when the hydride composition changes from $ZrH_{1.82}$ to $ZrH_{1.98}$. An abrupt decrease is observed for compositions greater than $ZrH_{1.90}$ until $ZrH_{1.94}$. For composition $ZrH_{1.94}$, maximum values for micro-hardness and brittleness have been reported previously [4].

The dependence of the specific void volume (V, cm^3/g) on the hydrogen content (Fig. 1b) for zirconium hydride of various grain sizes has a similar character. The smallest void volume is found for compositions near $ZrH_{1.90}$. The total amount of voids increases with increasing hydrogen content.

Analysis of the differential pore size dependencies for coarse grained material with composition $ZrH_{1.90}$ shows that the main fraction of the total volume of voids (85%) corresponds to pores with an effective radius of 1–30 μm. Such voids occupy only 59% of the total volume in hydride $ZrH_{1.98}$, and others have effective radii of 0.1–1.0 μm; this can be explained by the increase in the total amount of voids with increase of hydride composition due to the emergence of many small voids.

Ceramographic examination of coarse grain hydride confirms the essential changes of its structure and the presence of defects (Fig. 2).

A more regular structure is observed for compositions $ZrH_{1.82}$–$ZrH_{1.90}$ (Fig. 2a). Re-orientation of second-order twins with the formation of lamellae discontinuity and micro-cracks on the borders of re-orientated areas (Fig. 2b) is typical for compositions $ZrH_{1.92}$–$ZrH_{1.95}$. Micro-cracks also occur on sites where twins cross. When the hydrogen content is close to composition $ZrH_{1.95}$ and above, further development of micro-cracks with the formation of cavities–channels with a certain crystal orientation (Fig. 2c) takes place. Such cavities develop deep into the material with increasing hydrogen content, and for $ZrH_{1.98}$ can cover significant parts of the grain (Fig. 2d). Similar formation of multiple micro-cracks and packets of oriented channels in other brittle materials with a structure formed by polysynthetic twins has been reported [6,7]. The occurrence of such defects in ε-zirconium hydride is probably caused by changes in the twinning structure under stress due to material volume changes when hydrogen is introduced into the material.

The decrease in the strength of hydride $ZrH_{1.95}$ coincides with a significant increase in the amount of micro-cracks for this composition, which is the probable cause. Accelerated crack formation has been observed for $ZrH_{1.95}$ samples, which were characterized as being the most brittle [4].

4. Conclusion

These investigations have shown that the bending strength values change non-monotonously when the zirconium hydride composition changes from $ZrH_{1.82}$ to $ZrH_{1.98}$. The most marked decrease in strength is observed for composition $ZrH_{1.95}$, for which a significant increase in the number of defects is found. The main continuity defects in ε-zirconium hydride are micro-cracks and channels linked to elements of the twin structure.

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