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Quantitative determination of absorbed hydrogen in oxidised zircaloy by means of neutron radiography

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Abstract

Hydrogen absorbed in steam-oxidised zircaloy can be determined quantitatively by means of neutron radiography. Correlation parameters between the total cross section and hydrogen content as well as oxide layer thickness were determined quantitatively. At H/Zr atomic ratios lower than 1.0, linear correlations between the hydrogen content and total cross section exist. The total cross section of Zr is lower and the effect of the hydrogen is higher in radiography measurements with a cold neutron spectrum than with a thermal spectrum. A Be filter reduces the effects of lower wavelength and epithermal neutrons and extends the linear correlations to higher H/Zr atomic ratios. Due to the better possibilities of background corrections, the neutron image should be detected by a CCD camera for a proper quantitative analysis with a medium spatial resolution of about 0.1 mm. A higher spatial resolution, but larger uncertainties in the quantitative hydrogen determination are achieved by measurements with imaging plates.

The effect of oxygen layers on the total cross section is much smaller than the effect of hydrogen. The total cross section measured depends linearly on the oxide layer thickness.

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Keywords: Neutron radiography; Hydrogen absorption; Zircaloy; Cold neutrons; Thermal neutrons

1. Introduction

The loss-of-coolant scenario and the possibility of reactor cooling by re-flooding is the subject of recent research under the QUENCH programme of Forschungszentrum Karlsruhe, Germany [1–3]. The coexistence of hot fuel and cooling water results in a strongly exothermic steam oxidation of the fuel cladding, as a consequence of which hydrogen is released.

$$2H_2O + Zr \Leftrightarrow ZrO_2 + 2H_2. \tag{1}$$

The hydrogen may be released into the reactor environment, which causes the risk of hydrogen detonation. Part of the hydrogen may be stored at least temporarily, dissolved in the remaining zirconium of the cladding material or as hydrides:

$$H_{2(gas)} \Leftrightarrow 2H_{(abs)}. \tag{2}$$

In Ref. [4] the thermodynamic equilibrium conditions of Eq. (2) were investigated. Zircaloy specimens were annealed at temperatures between 800 and 1500 °C in argon/hydrogen atmospheres with varying hydrogen partial pressure. The absorption can be described well by Sieverts' law. Oxygen dissolved in the zircaloy decreases the hydrogen solubility significantly. In the phase diagram shown in Fig. 1 the equilibrium concentrations are given as a function of temperature for different hydrogen partial pressures in the environment.

In the case of water steam oxidation, a stable oxide layer is formed. Fig. 2 gives a metallographic image of an oxidized zircaloy tube segment. The solubility and diffusivity of hydrogen in ZrO_2 are very low. This oxide layer acts as a barrier for hydrogen transport from the atmo-

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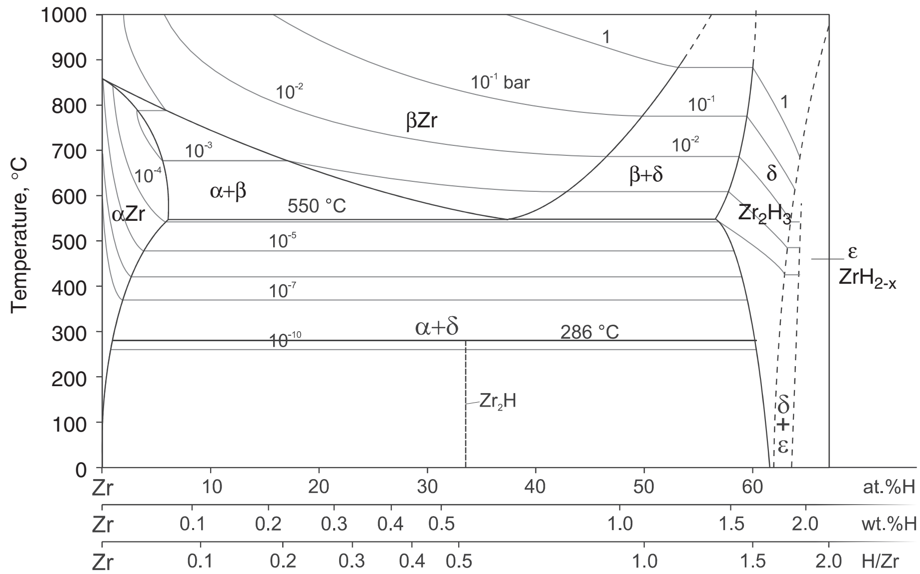

Fig. 1. Zr–H phase diagram with equilibrium concentration for different environment hydrogen partial pressures [6].

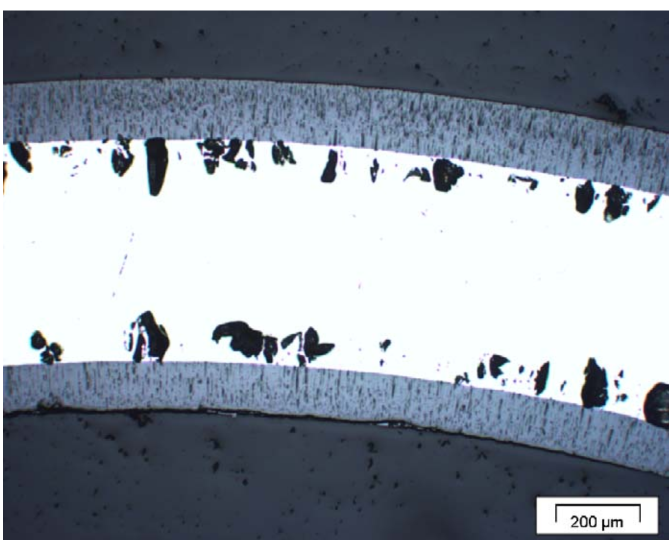

Fig. 2. Microstructure of steam-oxidised Zry-4 (1100 °C, 1 h) with outer oxide layer, α-Zr, prior β-Zr, α-Zr, and inner oxide layer.

sphere into the metal, but also from the metal into the atmosphere. Therefore, hydrogen absorption during steam oxidation is controlled not only by the hydrogen supplied from the atmosphere, but also by diffusion through the oxide layer. In Ref. [5] a kinetic model is given for this transport process. To determine the parameters of the model, the hydrogen content in the material after different steam oxidation treatments has to be known.

Usually, the hydrogen content is determined by measuring the composition of the off-gas during hot extraction. In Ref. [3] it is shown that 0.8% to 6% of the hydrogen produced is stored in the remaining metal.

This amount has less influence on the risk of hydrogen detonation, but it may strongly influence the mechanical behaviour of the damaged fuel rod cladding. However, the hot extraction method is destructive and does not provide any spatial resolution better than about some millimetres. No separation between the different phases (ZrO_2, α- or β-Zr) is possible.

Alternatively, neutron radiography experiments allow to non-destructively determine the hydrogen content with a spatial resolution better than 15 µm. In Refs. [7,8] this method was applied to qualitatively analyse hydrogen distribution in nuclear fuel rods after service. Hydride lenses were found. In Ref. [9] a quantitative relation between hydrogen concentration and a grey level in the neutron radiography image is given. Unfortunately, no information about transmissions and total cross sections of the specimens is supplied. Hence, the quantitative relations presented in this paper are valid only for the camera setup used. They cannot be transferred to other experimental setups.

The aim of this paper is to find relations which can be used for a quantitative determination of the hydrogen content of the different phases in steam-oxidised zircaloy based on non-destructive investigations.

2. Theoretical background

The contrast in the radiography image is caused by transmission differences of specimens differing in their hydrogen content and thickness. Assuming mono-energetic neutrons and scattering events acting like absorption, the transmission T is given by the exponential attenuation law:

$$T = \frac{I}{I_0} = \exp(-\Sigma_{\text{total}} \cdot s) \tag{3}$$

with I and I_0 denoting the neutron intensity behind and before the specimen, respectively, Σ_{total} being the total