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Hydride precipitation, fracture and plasticity mechanisms in pure zirconium and Zircaloy-4 at temperatures typical for the postulated loss-of-coolant accident

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HIGHLIGHTS

- All δ-hydrides in Zr and Zircaloy-4 have basal or pyramidal types of habit planes.
- Seven orientation relationships for δ-hydrides in Zr matrix were detected.
- Decohesion fracture mechanism of hydrogenated Zr was investigated by fractography.

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ABSTRACT

The results of investigations of samples of zirconium and its alloy Zircaloy-4, hydrogenated at temperatures 900–1200 K (typical temperatures for loss-of-coolant accidents) are presented. The analyses, based on a range of complementary techniques (X-ray diffraction, scanning electron microscopy, electron backscatter diffraction) reveals the direct interrelation of internal structure transformation and hydride distribution with the degradation of mechanical properties. Formation of small-scale zirconium hydrides and their bulk distribution in zirconium and Zircaloy-4 were investigated. Fractographical analysis was performed on the ruptured samples tested in a tensile machine at room temperature. The already-known hydrogen embrittlement mechanisms based on hydride formation and hydrogen-enhanced decohesion and the applicability of them in the case of zirconium and its alloys is discussed.

1. Introduction

Hydrogen can penetrate into the material of fuel rod claddings under normal reactor operation conditions (temperature below 700 K) in a relatively small amount (up to 400 wppm H for Zircaloy-4 at burn-up of 50 GWd/tU) (Gottuso et al., 2006). But during a loss-of-coolant accident (LOCA) the cladding undergoes sufficiently high temperatures (usually between 900 and 1200 K), to cause it to balloon and subsequently burst. The coolant water vapourised during the accident penetrates firstly through the oxide cracks in the ballooning region and (mainly) through the burst opening into the cladding and comes into contact with the non-oxidised inner cladding surface. The zirconium reacts with steam inside the tube and the hydrogen that is produced due to this type of oxidation would mostly be absorbed by the zirconium metal cladding material. The corresponding processes at the inner cladding surface describes the so-called secondary hydrogenation process during which high hydrogen concentrations up to 4000 wppm H can be locally reached as detected by Uetsuka et al. (1981) and investigated later by different research groups (Billone et al., 2008; Stuckert et al., 2013).

Zirconium hydrides form in claddings as soon as the terminal solid solubility of hydrogen in zirconium is exceeded (Fig. 1). This may happen in two different ways during operation when the concentration increases or in the cooling phase of the reactor core when temperature decreases. This would significantly increase the embrittlement of the cladding tubes.

Abbreviations: EBSD, Electron Backscatter Diffraction; LOCA, Loss-of-coolant accident; GWd/tU, Gigawatt-days/metric ton of uranium; wppm, Weight parts per million; TEM, Transmission Electron Microscopy; EDX, Energy dispersive x-ray spectrometry; XRD, X-ray diffraction analysis; QUENCH, Facility for performing the loss-of-coolant bundle tests at Karlsruhe Institute of Technology (KIT, Germany); LORA, Laboratory furnace for Reduced Atmospheres; ICP-OES, Inductively coupled plasma optical emission spectrometry; RD, Radial direction of the cladding tube; AD, Axial direction of the cladding tube; TD, Tangential direction of the cladding tube; NUSAFE, Nuclear Safety Research Programme at Karlsruhe Institute of Technology.

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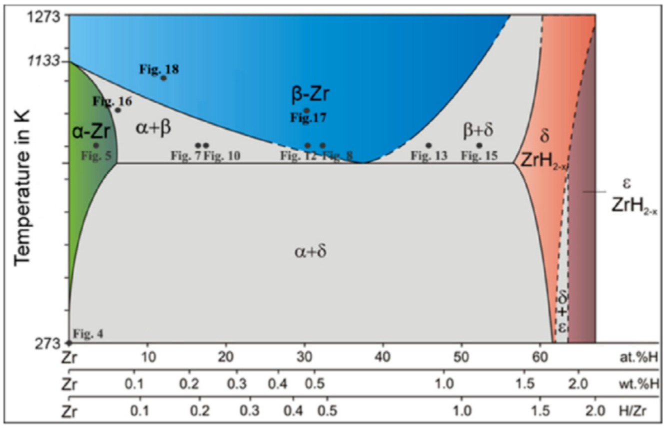

Fig. 1. Zr–H equilibrium phase diagram according to Zuzek et al. (1990) with points denoting hydrogenation tests.

During LOCA the temperature can reach the boundary of the phase transition of the Zr alloy. In the high-temperature β-phase the solubility of hydrogen is much higher, but after fast cooling (quenching) the oversaturated solid solution decomposes forming a special Widmanstätten pattern with two types of zones with redistributed dilute elements (Williams and Gilbert, 1966). The hydrides formed are of sub-micrometre dimensions and the chance of detecting hydrides in zirconium after this structure transformation by optical methods is quite low. Additionally, the acicular structure makes it difficult to analyse the hydride morphology and distribution.

A review of questions related to the habit planes of hydrides in zirconium and its alloys investigated by means of transmission electron microscopy (TEM) and metallography was published by Ells (Ells, 1968). A lot of hydride habit planes had been reported. Most of the investigators detected prismatic and near-basal $\{1\ 0\ \times\}_{\alpha\text{-Zr}}||\{1\ 1\ 1\}_{\delta}$ orientation relationships. Previously the basal plane as the possible habit plane for Zr hydrides was detected (Arunachalam et al., 1967). In contrast to optical methods TEM could give clearer information on hydride formation. The work of Chung supports the suggestion that basal plane is a habit plane for delta hydrides in α-Zr (Chung, 2000), but the main problem with this technique is the statistics which is usually low due to local region of TEM investigation. There are also a lot of complexities and uncertainties that can be introduced into the structure during preparation of a small and, if hydrogenated, very brittle specimen. Furthermore, the surface hydrides make the electrochemical polishing procedures difficult. Until now only specimens with low hydrogen content, hydrogenated in α-Zr phase field of the Zr–H phase diagram were used in TEM investigations. These could be the reason for controversial data on zirconium hydrides orientation relationships.

The method of electron backscatter diffraction analysis (EBSD) is used to obtain data on the lattice type and its orientation in a local volume at a scale of tens of nanometres. Subsequent scanning of the specially prepared surface allows constructing a phase map and an orientation distribution map over a hundred micrometre scale region, combing the resolution of TEM with a field of investigation that ranges over hundreds of material grains. This gives the investigator the necessary statistics and, therefore, improves the understanding. On the basis of neighbouring grain orientations, the information on grain boundary type and overall length of boundaries can be obtained. Such orientation maps are of great value for the analysis of material microstructure development due to external impact such as, for example, hydrogen uptake and hydride formation.

In spite of the enormous amount of publications on hydrogen uptake and hydride formation, only two research groups have achieved sufficient success in investigating zirconium hydrides by means of EBSD (Qin et al., 2014; Une et al., 2004). And no one has investigated the hydride distribution in a material in order to give comprehensive information on the type of hydride, their spatial distribution, their relation to the metal matrix and their lattice distortion combined with a fractographical analysis of embrittled material.

The first thorough EBSD analysis of zirconium alloy (Zircaloy-2) was done by Une et al. (2004). Delta-hydrides and their relation to zirconium matrix were investigated. Specimens were hydrogenated up to 250 wppm H in LiOH solution at 573 K. One of the most recent works on hydrogenated Zircaloy-4 were done by Qin et al. (2014). In this case also only δ-hydrides were detected using EBSD. Hydrogen content was approximately 500 wppm. The samples were hydrogenated under a temperature of 623 K and then cooled in furnace to room temperature. This paper of Qin and co-authors is of the great importance because the structural aspects and the interactions of the metal matrix with the hydride network were emphasised.

However, use of only the EBSD method is not enough to be sure that the phases that we detected are the phases of interest. This is especially relevant if there could be many types of hydrides (γ-, δ- and ε-hydrides) after hydrogenation. In this case X-ray diffraction (XRD) is the most powerful and accurate complimentary technique for phase analysis that helps to answer all the questions concerning phase detection.

To study the embrittlement due to hydrogen uptake, one needs methods that can clearly show whether new phases formed are brittle and this brittleness has significant impact on the overall material fracture behaviour and its resistance to brittle failure. This is possible by means of SEM fractography based on high resolution scanning electron microscopy of ruptured surface. The fracture surface would be that obtained after conventional tensile testing.

The problem of small-scale hydrides detection in Zr and its Zr–Sn alloys is obviously a challenge, as there have been no satisfactory data provided until this date. This should in addition be investigated by a range of complimentary techniques. No one to date has performed EBSD investigations of high hydrogenated zirconium or zirconium alloy, particularly in the LOCA temperature regime. Nevertheless, it is of great importance to know how and where hydrides would be formed and how would the embrittlement develop during LOCA-regimes. This necessity had already been emphasised in previous works (Pshenichnikov et al., 2015; Stuckert et al., 2013).

Thus, the main goal of this work is to provide the thorough analysis of specimens hydrogenated over a wide range of hydrogen contents from 400 to 12,550 wppm H by means of EBSD, XRD and SEM techniques. The field of investigation covers all possible hydrogenated structure types as it can be seen from Fig. 1 (all performed experiments are represented with points). Data obtained by means of such comprehensive analyse help (1) to detect hydrides, their morphology and distribution in different types of structure; (2) to establish crystallographic relationship between the Zr matrix and hydrides; (3) to detect the locations and interrelations between γ- and δ-hydrides; (4) to understand the mechanism of embrittlement. Additionally, the difference between hydride formation and their development in pure Zr and in the well-known technical alloy, Zircaloy-4, which is widely used in nuclear industry as reactor core material, was investigated. On the basis of the new data on explanation for the brittleness of the cladding tubes after the QUENCH–LOCA bundle tests (Stuckert et al., 2014) was made possible.