Nucl Eng Technol 47 (2015) 746–755

Available online at www.sciencedirect.com

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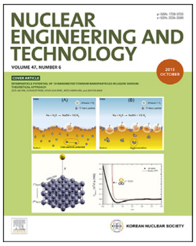
journal homepage: http://www.journals.elsevier.com/nuclear-engineering-and-technology/



Original Article

THE EFFECT OF HYDROGEN AND OXYGEN CONTENTS ON HYDRIDE REORIENTATIONS OF ZIRCONIUM ALLOY CLADDING TUBES

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A R T I C L E I N F O

Article history:
Received 4 April 2015
Received in revised form
26 June 2015
Accepted 26 June 2015
Available online 11 August 2015

Keywords:
Hydride precipitation
Hydrogen solubility
Mechanical property
Zirconium alloy

A B S T R A C T

To investigate the effect of hydrogen and oxygen contents on hydride reorientations during cool-down processes, zirconium–niobium cladding tube specimens were hydrogen-charged before some specimens were oxidized, resulting in 250 ppm and 500 ppm hydrogen-charged specimens containing no oxide and an oxide thickness of 3.8 μm at each surface. The nonoxidized and oxidized hydrogen-charged specimens were heated up to 400°C and then cooled down to room temperature at cooling rates of 0.3°C/min and 8.0°C/min under a tensile hoop stress of 150 MPa. The lower hydrogen contents and the slower cooling rate generated a larger fraction of radial hydrides, a longer radial hydride length, and a lower ultimate tensile strength and plastic elongation. In addition, the oxidized specimens generated a smaller fraction of radial hydrides and a lower ultimate tensile strength and plastic elongation than the nonoxidized specimens. This may be due to: a solubility difference between room temperature and 400°C; an oxygen-induced increase in hydrogen solubility and radial hydride nucleation energy; high temperature residence time during the cool-down; or undissolved circumferential hydrides at 400°C.

1. Introduction

During the interim dry storage of spent nuclear fuel, the fuel rod internal pressure can generate tensile hoop stress on the zirconium alloy cladding tubes that cool down very gradually from various cladding tube peak temperatures of between 200°C and 400°C over several decades. This interim dry storage condition may generate tensile hoop stress-induced hydride reorientation in the radial direction of the cladding tube and reduce the cladding's ductility. The aforementioned stress-induced hydride reorientation behavior in zirconium alloys has been investigated by many researchers [1–12]. Based on these research results, it can be said that the amount of radial hydrides formed during the interim dry storage period may be dependent on hydrogen solubility in the zirconium alloy cladding, heat-up cladding temperatures during the fuel dry

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http://dx.doi.org/10.1016/j.net.2015.06.004

period, tensile hoop stresses, cool-down rates, hydrogen contents, etc. In addition, it was reported that the formation of radial hydrides in the cladding tubes may be closely related to their fabrication histories, textures, and stress states [13–16].

However, sufficient data on hydride reorientation behaviors during cool-down have not been provided for spent fuel cladding conditions that simulate both oxygen and hydrogen contents as well as neutron irradiation-induced microstructure changes. It is noteworthy that the hydrogen solubility increased with the oxygen-containing Zircaloy-4 materials [17], while it increased in the lower oxygen content range but decreased in the higher oxygen content range [18]. In this study, therefore, the effect of both hydrogen and oxygen contents on the hydride reorientation behaviors, such as radial hydride fractions and lengths, was investigated along with various tensile hoop stresses and cool-down rates.

In general, a temperature limit of 400°C, which is specified for normal and short-term transient conditions during the interim dry storage, will limit cladding hoop stresses and the amount of dissolved hydrogen atoms available to precipitate hydrides during the cool-down [14]. It is generally recognized that the hydrogen content in cladding should be controlled to below 600 ppm-H and the fuel rod internal pressure should be controlled to below the reactor coolant system pressure (15.5 MPa) that may cause a tensile hoop stress of 150 MPa on the cladding tube during the interim dry storage period. It is also reported that the cladding may cool down over several decades by about 100°C per 10 years (2×10^{-5}°C/min) [19]. It is also noted that the zirconium–niobium (Zr-Nb) alloy cladding tubes have been used mostly for pressurized water reactors.

In this study, therefore, stress relieved annealed (SRA) Zr-Nb cladding alloys were employed. The test matrix included two hydrogen contents, one tensile hoop stress and two cooling rates, simulating the spent fuel conditions at the interim dry storage conditions. Firstly, based on the aforementioned allowable maximum hydrogen content of 600 ppm, two hydrogen contents of 250 ppm and 500 ppm in the SRA Zr-Nb tube specimens were used to evaluate the effect of hydrogen content on the hydride orientation behaviors. Secondly, the aforementioned maximum tensile hoop stress of 150 MPa was employed to evaluate the effect of the maximum tensile hoop stress on the hydride reorientation. Lastly, considering the expected slowest cooling rate 2×10^{-5}°C/min during the interim dry storage, two cooling rates of 0.3°C/min and 8.0°C/min were selected to evaluate the effect of cooling rate on the hydride reorientation. The Zr-Nb tube specimens were oxidized to 3.8 μm at their inner and outer surfaces to evaluate the effect of oxidation on the hydride reorientation. The specimens were heated up to 400°C with one heating rate of 3.0°C/min and then remained at that temperature for 2 hours to provide enough time for hydride dissolution prior to cool-down. The specimens were cooled down to room temperature with the respective cooling rates of 0.3°C/min and 8.0°C/min under the tensile hoop stress of 150 MPa.

2. Material and methods

Chemical compositions, texture and dimensions of the Zr-Nb cladding tubes used in the pressurized water reactors are given in Table 1. The Zr-Nb cladding tubes that were cold-pilgered and stress-relieved were supplied by the Korea Nuclear Fuel Company. These cladding tubes were cut into several parts of 100 mm each before the tube surfaces were cleaned with acetic acid. Two parts of the tubes were charged with hydrogen in a vacuum furnace at 400°C containing a mixture gas of hydrogen (150 mmHg) and helium (200 mmHg) to generate a uniform distribution of hydrogen through the tubes [20]. The hydrogen contents of the test specimens were analyzed by the LECO hydrogen analyzer RH600. Various hydrogen contents of the test specimens were generated, including 200 ± 20 ppm, 250 ± 20 ppm, 450 ± 20 ppm, and 500 ± 20 ppm. Only the hydrogen-charged specimens of 200 ppm and 450 ppm were oxidized for ~60 days at 360°C and 17.5MPa in an autoclave under the water atmosphere, resulting in about 3.8 μm at each surface of the test specimens. These oxidized hydrogen-charged specimens were found to contain respective hydrogen concentrations of 250 ± 25 ppm and 500 ± 25 ppm, indicating that hydrogen pickup occurred during the oxidation process in the autoclave. After heating up the oxidized specimens to 400°C and holding them at that temperature for 2 hours, the signal detector (SEM-EDS)–XFlash6 was employed to measure oxygen content in the metal region. Before the oxygen content measurements, the specimens were polished to remove any surface contamination. The oxygen atoms in the metal phase appear to be distributed nearly uniformly. The oxygen content in the metal phase were measured to be 2.0 ± 1.5 w/o (weight percent) for the oxidized specimens.

Fig. 1 shows a schematic configuration of the test specimen and two half-cylinder loading pins that open and strain the test specimen. The test specimens were cut transversely from the cladding tubes to make a width of 5 mm. The diameter of the half-cylinder loading pin is 8.35 mm and the gage length of the test specimens is 2 mm. Special grips were designed and fabricated to fix the loading pins and apply some load on the test specimen. As seen in Fig. 2, the test specimens were heated up to 400°C at 3.0°C/min and remained for 2 hours at that temperature. Then, the oxidized specimens were cooled down with two cooling rates of 0.3°C/min and 8.0°C/min under the tensile hoop stress of 150 MPa. The cooling rate of 0.3°C/

Table 1 – Zirconium alloy cladding tubes used in this work.

Materials	Chemical composition (w/o)	Texture (Kearns number)	Tube dimension (mm)
Zr alloy	Zr-1.0Nb-1.0Sn-0.1Fe-0.12O	f_r (radial) = 0.62 f_t (tangential) = 0.26 f_a (axial) = 0.12	Outer dia. = 9.50 Thickness = 0.57

Fe, iron; Nb, niobium; Sn, tin; w/o, weight percent; Zr, zirconium.