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Journal of Alloys and Compounds 389 (2005) 102–112

Journal of ALLOYS AND COMPOUNDS

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Terminal solid solubility of hydrogen in Zr-alloy pressure tube materials

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Received 26 May 2004; received in revised form 29 July 2004; accepted 29 July 2004

Abstract

In this work, terminal solid solubility (TSS) of hydrogen for Zr-alloy pressure tube materials was determined corresponding to end of hydride dissolution (TSSD) and start of hydride precipitation (TSSP) using the dilatometry technique. For this, Zircaloy-2 and Zr–2.5Nb pressure tube alloy coupons were gaseously charged with controlled amount of hydrogen in the range 10–100 μg/g. Change in length of cylindrical specimens of length ∼10 mm and diameter ∼3.5 mm machined from the coupons were measured as a function of temperature using a dilatometer. The samples were heated at 2 °C/min to 430 °C, held for 30 min at 430 °C and cooled back to the ambient temperature at 2 °C/min. The transition temperatures corresponding to the end of dissolution of hydrides during heating and beginning of precipitation of hydrides during cooling in these alloys were determined from thermal strain (e) versus temperature (T), average slope (of e versus T plot) versus T and differential thermal strain versus T plots. The enthalpies of hydride dissolution and precipitation for Zircaloy-2 pressure tube material were found to be 30–34.5 and 25.9–26.3 kJ/mol, respectively, whereas the corresponding enthalpies for Zr–2.5Nb pressure tube material were found to be 35.44 and 17.2–22.8 kJ/mol, respectively. This difference in the enthalpies between TSSD and TSSP is explained in terms of the different roles played by the components of strain energy associated with the elastic and plastic deformation in the matrix and precipitate, as a result of hydride accommodation in this alloy during heating and cooling process.

Keywords: Precipitation; High temperature alloys; Thermal analysis; Zircaloy-2; Zr–2.5Nb alloy; Dilatometry

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1. Introduction

Dilute zirconium alloys are used as the core structural materials of pressurized heavy water reactors (PHWR) because of their low neutron absorption cross-section, good elevated temperature mechanical properties and adequate aqueous corrosion resistance [1–7]. Though the hydrogen content of the in-core components is kept as low as possible by controlling the manufacturing process parameters [8], it can pick up hydrogen/deuterium during service from corrosion reaction between zirconium metal and coolant heavy water [7–12]. Hydrogen present in excess of solid solubility precipitates out as brittle hydride phase [13–21] and can severely limit the life of core components [22–24] made up of these alloys. The hydrogen-related problems associated with these components are hydride embrittlement [22–24] which gets aggravated due to stress-reorientation of hydride [25–31], delayed hydride cracking (DHC) [30–36] and hydride blister formation [30,37–41]. Initially, TSS was thought to be a safe limit for hydrogen concentration, below which embrittlement effect was not considered significant. However, recent studies have shown that the threshold hydrogen concentration for DHC initiation [32,36] and hydride blister nucleation [41,42] are not TSS but a fraction of TSS. Thus, terminal solid solubility of hydrogen in these alloys is an important parameter and is used by design and safety engineers for fitness for service assessment of these components [43].

Experimentally TSS is determined by preparing samples with known concentration of hydrogen and measuring some change in physical properties to identify transition temperature corresponding to end of hydride dissolution during heating and beginning of hydride precipitation during cooling. Techniques like dilatometry [44,45], resistivity [46], internal

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doi:10.1016/j.jallcom.2004.07.048

friction [47–49], differential scanning calorimetry [50–53], small angle neutron scattering [54,55], metallography [56] and thermal diffusion [57] measure changes in dimension, resistance, damping frequency, heat flow, lattice parameter, microstructural features and H concentration, respectively, and are used to determine the transition temperature. The experimentally determined transition temperatures are correlated with corresponding hydrogen concentrations in the form of an Arrhenius type relationship to obtain the pre-exponential constant and the enthalpy of the dissolution or precipitation process. With the help of these constants, TSS at any temperature can be obtained. Also, for a sample of unknown hydrogen concentration by determining the transition temperature corresponding to heating and/or cooling total hydrogen content of the sample can be estimated using the aforementioned constants.

Two series of dilute Zr alloys are being extensively used as pressure tube material in PHWR type reactors. Early generation PHWRs use tubes made of Zircaloy-2, an alloy with tin as primary alloying addition. Although pressure tubes of this material served satisfactorily in reactor applications, it is now known that Zircaloy-2 suffers from high rates of hydrogen pick up and somewhat high rates of irradiation induced creep [58]. The next important alloy is Zr–2.5 wt.% Nb (Zr–2.5Nb) [5–8,58] that has been chosen as a pressure tube material for new generation PHWRs. The Zr–2.5Nb alloy has been tried in two different conditions: conventional cold work and stress relieved and heat treated (quenched and tempered) state [59]. The microstructure of cold worked and stress relieved (CWSR) Zircaloy-2 consists of elongated and textured α Zr-phase (having hcp crystal structure) grains with a small amount of randomly distributed fine intermetallic precipitates [1–5]. On the other hand the microstructure of CWSR Zr–2.5Nb alloy is comprised of heavily elongated and strongly textured α phase grains surrounded by very thin but nearly continuous grain-boundary network of metastable β phase (having bcc crystal structure with 10–20% Nb and volume fraction in the range of 10–20%) [1–6,53,60]. McMinn et al., based on their investigations of a series of Zircaloys [61], have observed negligible influence of chemical composition and microstructure on TSS. Khatamian [52,53] investigated the TSS and partitioning of hydrogen in a series of Zr–Nb alloys in metastable (containing β-Zr with 20% Nb) and aged (containing β Nb with greater than 85% Nb) condition and has reported increase in hydrogen solubility for metastable alloy with increasing Nb content (or increasing β phase volume fraction). However, for the completely aged Zr–Nb alloys, TSS values were comparable to that for Zircaloys [52].

Thus, it is felt that the TSS of hydrogen in Zr–2.5Nb alloy pressure tube material containing metastable β-Zr phase must be higher compared to that for Zircaloys. The objective of this study is to determine the TSS of hydrogen in CWSR Zircaloy-2 and Zr–2.5Nb pressure tube materials used in the Indian PHWRs. Hydride precipitation in Zr-alloys is associated with a large positive volume change. One of the consequences of this large volume change is the local deformation of the matrix to accommodate the hydride precipitates. Based on the strain energy associated with elastic and plastic deformation of the matrix, Puls [33,59] developed a theoretical model of TSS of hydrogen in Zr-alloys. Experimentally observed values of TSS show large hysteresis between the values obtained during heating and cooling. TSS obtained during heating corresponds to the end of hydride dissolution and is called TSSD whereas TSS obtained during cooling corresponds to the beginning of hydride precipitation and is called TSSP. In this work both TSSD and TSSP values determined using dilatometry technique are discussed for Zr-alloy pressure tube materials.

2. Experimental

The Zircaloy-2 and Zr–2.5Nb pressure tube material was received from Nuclear Fuel Complex, Hyderabad, in autoclaved (cold worked and stress-relieved) condition. Typical chemical compositions of Zircaloy-2 and Zr–2.5Nb tubes are given in Table 1 [63]. Coupons of length 50 mm, width 20 mm were cut from the tube and were polished up to 1200 grit emery paper to obtain oxide free surface. The polished samples were gaseously charged with controlled amount of hydrogen in a modified Sieverts' apparatus [51,64]. In the present set of investigations, the samples were furnace cooled after hydrogen charging at 363 °C with an average cooling rate of ∼2 °C/min. To reveal the hydride morphology, orientation and distribution, the gaseously charged samples were sectioned along the radial-circumferential and axial-radial plane of the tube and metallographically examined under optical microscope. Before examination under optical microscope, the Zircaloy-2 samples were chemically etched by swabbing for 30 s with cotton soaked in 8% HF in HNO_3 solution [24] while the Zr–2.5Nb samples were etched by swabbing for 20 s with cotton soaked in 10%HF + 45%HNO_3 + 45%H_2O solution.

Table 1
Typical chemical composition of Zircaloy-2 and Zr–2.5Nb alloy pressure tube material depicting the weights of constituent alloying elements in percent [63]

Elements	Zircaloy-2	Zr–2.5%Nb
Tin	1.20–1.70	–
Iron	0.07–0.20	–
Chromium	0.05–0.15	–
Nickel	0.03–0.08	–
Niobium	–	2.40–2.80
Total Fe + Cr + Ni	0.18–0.38	–
Total Fe + Cr	–	–
Carbon (ppm)	150–400	–
Oxygen (ppm)	900–1400	900–1300
Copper	–	–
Zr + permitted impurities	Balance	Balance