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Letter to the Editor

Mitigation of hydride embrittlement of zirconium by yttrium

I.S. Batra [a], R.N. Singh [b,*], P. Sengupta [a], B.C. Maji [a], K. Madangopal [a], K.V. Manikrishna [a], R. Tewari [a], G.K. Dey [a]

[a] *Materials Science Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Mumbai 400085, India*
[b] *Mechanical Metallurgy Section, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Mumbai, Maharashtra 400085, India*

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ABSTRACT

Brittle hydrides of plate-shaped morphology are known to embrittle the host zirconium matrix. The embrittlement effect is a strong function of the aspect ratio of hydride plates and their major dimension, as thinner plates behave akin to cracks resulting in stress-concentration around their edges, especially when tensile load is acting normal to the broad face of the plates. The embrittlement of the host matrix is due to loss in load bearing area as a result of cracking of the hydride plates under load and severe localized deformation of the ligaments joining the hydride plates. In this work, mitigation of hydride embrittlement was attempted by exploiting the synergistic effect of yttrium addition to zirconium and microstructural modification of the Zr–Y alloy by quenching. This was expected to enable creation of a very high density of nucleation sites much stronger than those available otherwise and, thus, facilitate precipitation of much smaller hydrides that do not embrittle the host matrix. The results obtained in the present work on a dilute Zr–Y alloy do support this idea.

1. Introduction

Dilute Zr-alloys are used as pressure boundary for hot coolant in PHWR and RBMK reactors [1,2]. These pressure boundary components are subjected to aqueous corrosion leading to hydrogen/deuterium ingress into these components during service. The maximum amount of hydrogen that can be retained in solid solution without precipitation of hydrides is called terminal solid solubility (TSS) [3–5]. Hydrogen in excess of solid solubility causes precipitation of plate-shaped brittle hydride phase, which makes the pressure boundary components like pressure tubes of the aforementioned reactors susceptible to hydride induced embrittlement [6]. Two forms of hydride embrittlement (HE) have been recognized for hydride forming metals, namely, gross and localized [7]. The former requires certain minimum volume fraction of the hydride phase, and it results in overall reduction in tensile ductility, impact and fracture toughness. Gross embrittlement is strongly influenced by the orientation of hydride plates since the plates that are oriented normal to tensile load can significantly enhance the degree of embrittlement by providing an easy path for the growth of cracks through the hydrides [8].

Hydrogen in solid solution is not reported to cause embrittlement of Zr-alloys [9]. Hence, TSS at the operating temperature can be considered as a safe hydrogen concentration limit, even though, for localized form of hydride embrittlement, safe hydrogen concentration limit is just a fraction of TSS [10]. Considering the fact that the rate of hydrogen pick-up in present generation Zr-alloys is less than 1 ppm per year for these components [2], any effort to increase the TSS even by a few ppm would surely enhance the safe hydrogen concentration limit and, thereby, the life of these components. Therefore, the first objective of this work was to look for an alloying addition, in which, intrinsically, the solid solubility for hydrogen is high. Yttrium is known [11] to have TSS that is about two orders of magnitude higher than that for zirconium at a given temperature. It has earlier been tried as a getter [2] for hydrogen and, in conjunction with other elements, as an alloying addition to mitigate HE [12].

Large hydride plates are likely to enhance the degree of embrittlement by causing stress-concentration at the edges of hydride plates and severe localized plasticity of ligaments joining these hydride plates. It may be worthwhile to note that RBMK tubes of Zr–2.5 wt% Nb alloy, which are produced by quenching followed by ageing (Q&A), exhibit smaller hydride plates under optical microscopy as compared to those observed in cold-worked and stress-relieved (CWSR) tubes of the same material for identical hydrogen concentration [13]. Also, for the same concentration of hydrogen, in contrast to CWSR tubes, Q&A tubes exhibit a higher hydride plate number density. In case of CWSR tubes, α-grains are elongated. The preferentially aligned grain boundaries in these act as the nucleation sites for hydrides [14]. Manufacturing of Q&A tubes imparts in them a microstructure that comprises of Widmanstätten α-grains and very fine β-grains [15]. Apart from grain boundaries, sub-grain boundaries and inter-lath boundaries also act as the nucleation sites in these, which probably explains the observed smaller size of the hydride plates and their higher number density in the RBMK tubes. This prompted us to make an attempt to somehow increase the density of relatively stronger nucleation sites so

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[*] Corresponding author. Tel.: +91 22 25593817; fax: +91 22 25505151.
E-mail address: rnsingh@barc.gov.in (R.N. Singh).

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that hydrides that finally result due to their nucleation and subsequent growth turn out to be smaller for a given concentration of hydrogen in the alloy.

To meet the objective of suppressing HE by creating a rather large number of very small hydrides, and, possibly, increased TSS, yttrium was selected as an alloying addition for zirconium. The fact that yttrium has much higher solubility of hydrogen than zirconium at room temperature and is also a much stronger hydride former suggests that addition of yttrium to zirconium might achieve this objective. In the case of third generation Oxide Dispersion Strengthened (ODS) F/M steel [16] being developed the world over as a structural material for the first wall of a prototype 'Tokamak', Y–Ti–O complexes in this steel are expected to act as sites for the nucleation of bubbles of Helium at a high temperature of about 700 °C. Helium is produced in the steel due to the (n, α) reactions taking place in the steel due to its irradiation by the 14.1 MeV neutrons from the plasma. However, because of the very high density of these complexes ($>10^{23}$ complexes/m^3) created in this steel during its manufacturing, the bubbles are likely to grow only to nano sizes even for rather large contents of Helium that are likely to be generated during the life time of these prototypes. This strategy is likely to help solve the issue of high temperature Helium embrittlement of this steel. Since dilute Zr-alloys used in nuclear industry contain rather large amounts of oxygen (about 1000 wt ppm), yttrium, once it is added to the zirconium matrix, can form Y–Zr–O complexes by internal oxidation. These could then probably act as strong sites for the nucleation of hydrides at room temperature. Grain substructure produced by quenching does generate subgrain/lath boundaries which further add to the density of available nucleation sites resulting finally in extremely small hydrides even for very high concentrations of hydrogen in the alloy. This to us appears to be a step forward in the direction of addressing issues related to HE of zirconium alloys.

2. Experimental

A master Zr–Y alloy, containing 10 wt% Y, was prepared from iodide zirconium and yttrium using electron beam melting technique. Zr–0.5 wt% Y alloy button was produced by melting together nuclear grade sponge zirconium produced by Kroll's process and the master alloy in an appropriate proportion in an electric arc furnace. Repeated melting was carried out to ensure chemical homogeneity. The Zr–Y alloy button thus prepared and the arc melted sponge Zr button were encapsulated separately in mild steel jackets and hot-rolled at 1073 K to break the cast structure, which was followed by air cooling to ambient temperature. The hot-rolled material (about 1 mm thick) from the Zr–Y alloy as well as sponge Zr was sheared to obtain smaller pieces for water-quenching, hydrogen charging and metallography. Some of the hot-rolled pieces of both the alloy and the sponge Zr were charged with hydrogen in a modified Sievert's apparatus [7]. The remaining pieces were sealed separately in quartz tubes in Helium and heated to appropriate quenching temperatures, soaked for 30 min and then water quenched without breaking the quartz capsules. The quenching temperature of 1423 K for Zr–0.5 wt% Y alloy was chosen so as to have all the yttrium in solid solution. The quenching temperature for sponge Zr was selected as 1173 K to ensure quenching from β-Zr phase. The quenched samples were also charged with controlled amounts of hydrogen in the same apparatus [7]. Heat-treatment conditions and hydrogen content of the samples used in this study are listed in Table 1.

Metallography was carried out using a solution of HF, HNO_3 and H_2O in a proportion of 2:9:9 (by volume). The samples were characterized using optical microscopy, Electron Beam Micro Analyzer (EPMA), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS) and X-ray diffractometry. Hydrogen content in the samples was determined by Inert Gas Fusion (IGF) technique and hydride dissolution and precipitation temperatures were determined using Differential Scanning Calorimetry (DSC). For DSC scans, the samples were heated from ambient to 973 K at 10 K/min and cooled back at the same rate.

3. Results and discussion

Two sets of micrographs have been used to illustrate the efficacy of our approach, namely, addition of yttrium to zirconium followed by the quenching treatment, in mitigating HE. First set of micrographs pertains to Zr sponge. Micrographs obtained from the planes containing the rolling and thickness directions are shown in Fig. 1. The microstructure of the hot-rolled Zr charged with hydrogen (Zr-HR) exhibited large hydride plates, aligned preferrentially along the rolling direction (dark lines in Fig. 1(a)). The microstructure of hot-rolled Zr subjected to the quenching treatment (Zr-HRQ) is shown in Fig. 1(b). Usually it is difficult to etch both the hydrides and the grain boundaries simultaneously in Zr-alloys. Despite this, the contrast in Fig. 1(b) suggests that the hydrides are located at the grain boundaries. Due to the quenching treatment, the grains were equiaxed and hydrides did not show any preferred alignment relative to the rolling direction.

Second set of micrographs pertains to Zr–0.5 wt% Y alloy. Firstly, it was observed that the size of the hydride plates as seen under optical microscope for ZrY-HR sample (Fig. 2(a)) was much smaller than that in Zr-HR (Fig. 1(a)). Still more surprising observation was made in the case of the ZrY-HRQ samples (Fig. 2(b)). The microstructural features were very fine and the optical intensity contrast was not able to reveal the presence of hydrides even for hydrogen content as high as 1000 wppm. Since these samples did not reveal hydrides under the optical microscope, they were further characterized by X-ray diffraction to identify the phases present in this alloy and differential scanning calorimetry (DSC) to identify hydride dissolution and precipitation temperatures.

DSC analysis of the ZrY-HRQ sample, indicated dissolution and precipitation temperatures of 834 K and 778 K, respectively, that are comparable to dissolution and precipitation temperatures of hydrides in dilute Zr-alloys containing about 600 wppm of hydrogen [17]. Since the martensitic structure which formed on quenching is metastable and so could have been the nucleation sites created by the combination of alloying and quenching employed in the present work, it was thought that, probably, the thermal treatments imparted during DSC scans up to 973 K may alter the microstructure as well as the size of the re-precipitated hydrides. However, interestingly, light microscopy of the samples that had

Table 1
Heat-treatment conditions and hydrogen content of the samples used in this study.

Material	Hot-rolling temperature, K	Quenching temperature, K	Hydrogen content, wppm	Sample Id.
Zr-sponge	1073	No quenching	400	Zr-HR
Zr-sponge	1073	1173	400	Zr-HRQ
Zr–0.5 wt% Y	1073	No quenching	400	ZrY-HR
Zr–0.5 wt% Y	1073	1423	1000	ZrY-HRQ

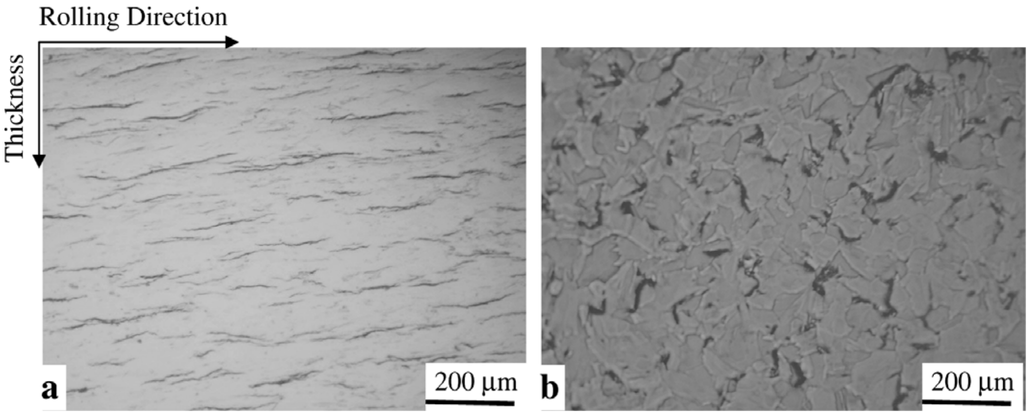

Fig. 1. Microstructure of (a) hot-rolled zirconium charged with 400 wppm of hydrogen (Zr-HR) showing hydrides (dark lines) aligned preferentially along the rolling direction and (b) hot-rolled zirconium quenched from 1173 K and charged with 400 wppm of hydrogen (Zr-HRQ) showing hydrides at the grain boundaries (dark phase).

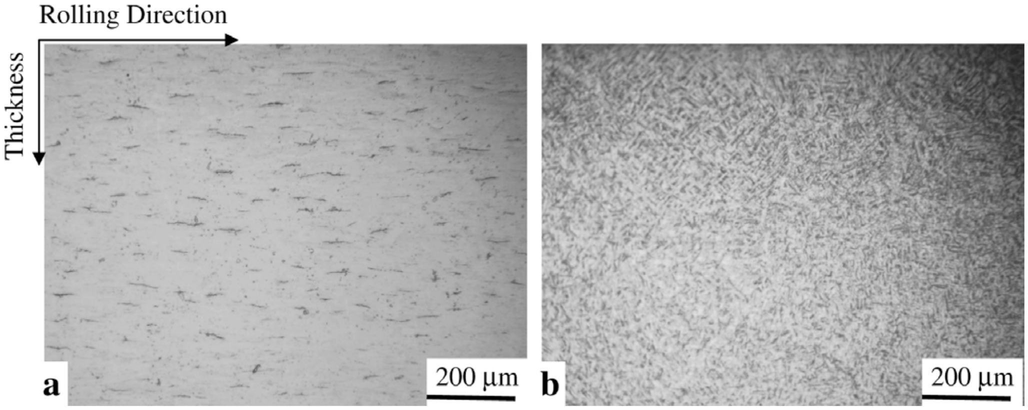

Fig. 2. Microstructure of (a) Zr–0.5 wt% Y alloy, hot-rolled and charged with 400 wppm hydrogen (ZrY-HR) and (b) Zr–0.5 wt% Y alloy, hot-rolled, quenched from 1423 K and then charged with ~1000 wppm of hydrogen (ZrY-HRQ). No hydrides were revealed under the microscope in the case of ZrY-HRQ sample.

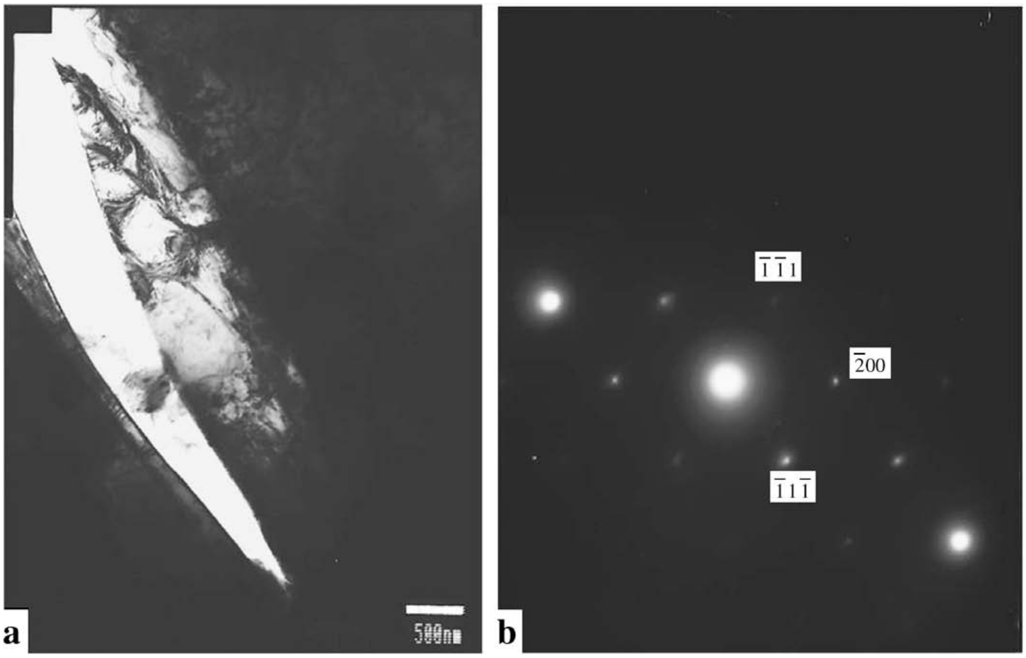

Fig. 3. TEM micrograph (a) of Zr–0.5 wt% Y alloy in ZrY-HRQ sample showing largest observed δ-hydride (maximum thickness 800 nm) and its SADP (b) having zone axis of [011].

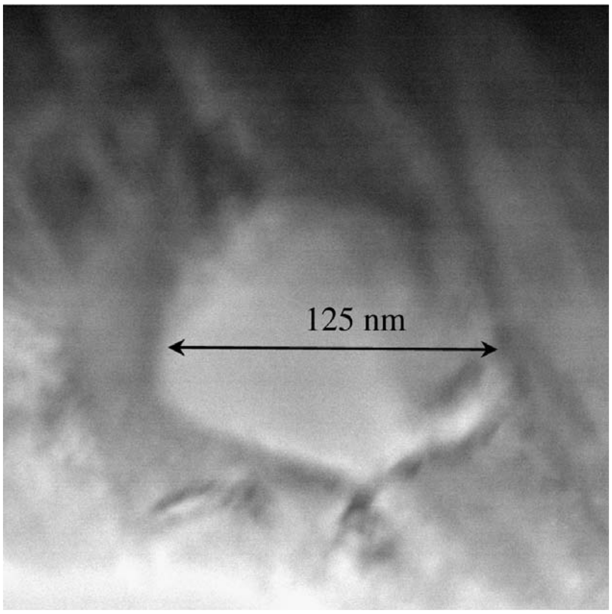

Fig. 4. TEM (BF) image of a 125 nm particle in Zr–0.5 wt% Y alloy in ZrY-HRQ condition.

Table 2
Composition of particles in ZrY-HRQ sample.

Element	wt% in particle
Zr	96.91
Y	2.18
O	0.89

been subjected to two consecutive DSC runs did not reveal any hydrides indicating thereby the thermal stability of the nucleation sites introduced and their efficacy in preventing the formation of large hydrides. Surprisingly, X-ray diffraction of the ZrY-HRQ sample revealed intensity peaks at 2θ angles that could be indexed in terms of δ-hydride phase. It may be noted here that even though the optical microscopy of this sample did not reveal hydrides, X-ray diffraction results indicated the presence of the δ-hydride phase. This observation suggests that hydride plate size is, perhaps, extremely small. This was also corroborated by Transmission Electron Microscopy (TEM) of the samples, which revealed the presence of very small hydride precipitates. One such δ-hydride, the biggest that could be seen in the sample under TEM, is shown in Fig. 3 with its Selected Area Diffraction Pattern (SADP). Another interesting observation that was made during these TEM investigations related to the occasional presence of 100–200 nm dia spherical particles. The lattice parameter of these particles was found to be near that of yttria. EPMA line-scan of the ZrY-HRQ sample revealed occasional yttrium peaks suggesting segregation of yttrium. The EDS scan of the TEM sample in ZrY-HRQ condition exhibited a uniform distribution of yttrium in the matrix. The EDS was also used to analyze the composition of the 100–200 nm spherical particles. One such particle, whose Bright Field (BF) image is shown in Fig. 4, was found to have the composition given in Table 2. This indicates towards the formation of Zr–Y–O complexes. The scavenging of oxygen by yttrium in the process of formation of these complexes could probably be considered responsible for the observed reduction in micro-hardness (at 200 gm load) from 230 VHN for Zr-HR to 215 for ZrY-HR. Looking at these results, it appears that yttrium in Zr in as small a quantity as 0.5 wt% coupled with quenching does facilitate precipitation of hydrides in extremely small sizes for even very large contents of hydrogen in these dilute binary alloys.

4. Conclusions

This work on Zr–0.5 wt% Y alloy indicates that yttrium as an alloying element coupled with quenching has the potential for mitigating HE in Zr-alloys. The nucleation sites introduced, because of their large number density in the quenched condition of the alloy, allow formation of extremely small hydrides even at rather large concentrations of hydrogen. This coupled with the obvious inherent capability of Zr–Y alloys to allow higher concentrations of hydrogen in solid solution may be exploited to enhance the life of the pressure tubes.

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