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Temperature dependence of misfit strains of δ -hydrides of zirconium

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Abstract

The misfit strains of both the isotopic forms of zirconium hydrides, viz., δ -ZrH_x and δ -ZrD_x, precipitated in zirconium were computed in the temperature range of 298–773 K and for $1.5 \leq x \leq 1.7$, using the methodology proposed by Carpenter. Misfit strains along (0001) plane and normal to it were observed to increase with increase in temperature for both the isotopic forms of hydrides. For a given isotopic atomic fraction, the misfit strains for deuteride were smaller than the corresponding values for hydride and with increase in atomic fraction of hydrogen isotopes, the misfit strains increased.

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1. Introduction

Apart from satisfying the generic requirements of the structural materials like good corrosion resistance and adequate high temperature strength and ductility under operating conditions, dilute Zr-alloys meet the specific requirements of the nuclear structural materials such as low neutron absorption cross-section, and microstructural and irradiation stability, required for application as core structural components in water-cooled nuclear reactors [1–3]. During normal operating conditions, the material is exposed to operating temperature under stress and is subjected to aqueous corrosion and irradiation damage. One of the consequences of the aqueous corrosion is the release of the hydrogen (H) or its isotope deuterium (D), a part of which is picked up by the material. Hydrogen in excess of solid solubility precipitates out as brittle hydride phase and makes the host matrix susceptible to embrittlement.

Misfit strains govern the strain energy associated with the accommodation of hydrides in α -Zr matrix [4], which is reported

to be the basis for the large hysteresis associated with terminal solid solubility of hydrogen in Zr-alloys [5,6]. Misfit strains, also called stress free transformation strains or dilatational strains, is an important parameter in theoretical modeling of hydride embrittlement phenomena [7] such as stress-reorientation [8], delayed hydride cracking (DHC) [9] and hydride blister formation [10]. Using room temperature lattice parameter of hexagonal close packed (hcp) α -Zr [11] and face centered cubic (fcc) δ -ZrH_{1.66} [12], Carpenter [13] calculated the dilatational misfit strains of zirconium hydride precipitated in zirconium. However, the lattice parameter of both α -Zr [14] and δ -ZrH_x [15] is reported to be influenced by temperature and composition [15,16], and hence is likely to influence the stress free transformation strains. Also, for a given concentration of hydrogen isotope, the lattice parameter of δ -ZrD_x [16] is reported to be smaller than that of δ -ZrH_x [15], suggesting that the misfit strains associated with accommodation of δ -ZrD_x [16] could be smaller than that for δ -ZrH_x [15].

The objective of this work is to determine the misfit strains for zirconium hydrides valid over a range of temperature and composition. The temperature dependence of misfit strains of δ -ZrH_x and δ -ZrD_x were determined from the lattice parameters of α -Zr [14], δ -ZrH_x [15] and δ -ZrD_x [16] in the temperature range of 298–773 K and for $1.5 \leq x \leq 1.7$. We have used the methodology proposed by Carpenter [13] to compute the mis-

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fit strains. Though under normal operating condition Zr-alloy components are exposed to temperatures around 573 K, under accidental condition it may be exposed to higher temperatures. Also, misfit strains at higher temperature are required to rationalize the threshold stress for reorientation of hydrides [7] and DHC velocity data [17] reported in literature at temperatures higher than 573 K. It may be noted that the lattice parameter of δ -ZrH_x [15] and δ -ZrD_x [16] are available only in the temperature range of 298–573 K and hence were extrapolated in order to determine the misfit strains at higher temperatures. The misfit strain data reported in the present work is valid for the temperature range of reactor operation and can be used in refining various hydride embrittlement models [8–10], i.e. to enhance the accuracy of model predictions.

2. Lattice parameter

The lattice parameters of hcp α -Zr single crystal were measured in the temperature range from ambient to 1133 K by Lloyd [14] using dilatation interferometry, which gives changes in dimensions and not the absolute value. Hence, Lloyd [14] used the ambient temperature lattice parameter values reported by Lichter [11] for reference. The polynomial expression, represented by Eqs. (1)–(4), describes the variation in lattice parameter of α -Zr [11,14], fcc δ -ZrH_x [15] and fcc δ -ZrD_x [16] with temperature in the temperature range of 298–773 K.

$$a^{\alpha\text{-Zr}} = 0.323118 + 1.6626 \times 10^{-6}(T - 298) \quad (1)$$

$$c^{\alpha\text{-Zr}} = 0.514634 + 4.7413 \times 10^{-6}(T - 298) \quad (2)$$

$$a^{\delta\text{-H}} = 0.4706 + 4.382 \times 10^{-3}x_{\text{H}} + \{2.475 \times 10^{-6} + 6.282 \times 10^{-6}x_{\text{H}} + 5.8281 \times 10^{-8}(x_{\text{H}})^2\}(T - 298) \quad (3)$$

$$a^{\delta\text{-D}} = 0.4738 + 1.961 \times 10^{-3}x_{\text{D}} + \{2.492 \times 10^{-6} + 6.3119 \times 10^{-6}x_{\text{D}} + 2.6081 \times 10^{-8}(x_{\text{D}})^2\}(T - 298) \quad (4)$$

where, a and c are the lattice parameter in nm, the superscript over a and c represent the phase, T is temperature in K, x is the atomic fraction of hydrogen or deuterium with $1.5 \leq x \leq 1.7$ and the symbols H and D representing the corresponding hydride

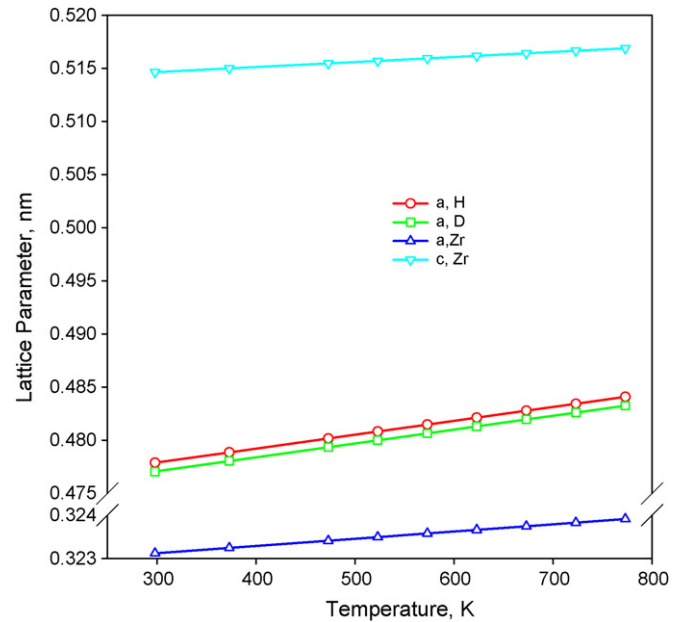


Fig. 1. Temperature dependence of lattice parameters of hcp α -Zr [14], fcc δ -ZrH_{1.66} [15] and fcc δ -ZrD_{1.66} [16].

or deuteride phase, respectively. The temperature dependence of the lattice parameter of α -Zr [14] and generally accepted composition of δ -hydride (ZrH_{1.66}) [15] and δ -deuteride (ZrD_{1.66}) [16] is shown in Fig. 1. It is evident from this figure that the lattice parameter of α -Zr [14] along c -axis shows stronger temperature dependence compared to that along a -axis. Also, the lattice parameter of δ -ZrH_{1.66} [15] is marginally greater than that of δ -ZrD_{1.66} [16] even though their thermal expansion coefficients are comparable.

3. Atomic radii

Since the α -Zr has hexagonal close packed crystal structure with $(c/a) < 1.633$, Zr atoms can be thought to be an ellipsoid [13] with semi-major axis r_{11} in the basal plane and semi-minor axis r_{22} normal to basal plane as illustrated in Fig. 2. As depicted in Fig. 2(a), Zr atoms can be thought to be in contact with its six nearest neighbours in the basal plane at a distance of $a^{\alpha\text{-Zr}}/2$,

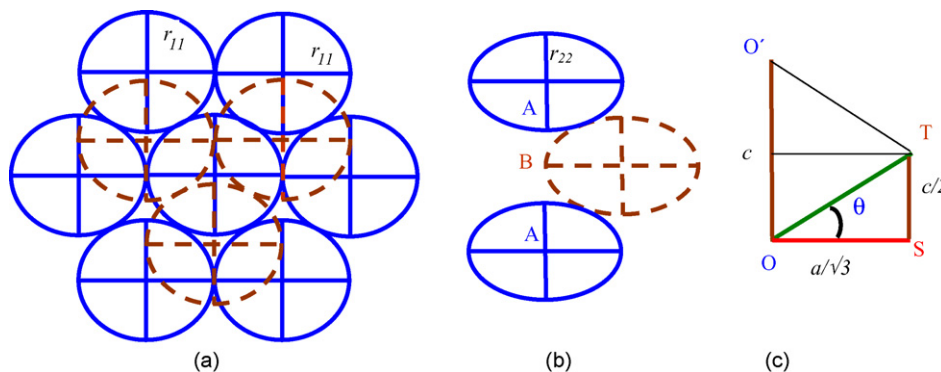


Fig. 2. Illustration of packing sequence and shape of α -Zr atoms. Projection of Zr atoms on basal plane will be circular (a) whereas when viewed from prismatic plane it will appear as an ellipsoid (b). Solid circles or ellipsoids represent atoms in layer A and dashed circles or ellipsoids represent atoms in layer B. Points O, O' and T are the centre of Zr atoms (c).

which implies that $r_{11} = a^{\alpha\text{-Zr}}/2$. Also, every Zr atoms in the basal plane will be in contact with three Zr atoms each above and below the basal plane at a distance of $1/2\sqrt{((a^{\alpha\text{-Zr}})^2/3) + ((c^{\alpha\text{-Zr}})^2/4)}$. This has been shown by dotted circles in Fig. 2(a) with elliptical shape of the Zr atoms depicted in Fig. 2(b). Following simple geometrical calculation using the sketch shown in Fig. 2(c) the coordinates of point of contact between the Zr atoms in the basal plane and above it is computed and fitting the coordinates in the equation of ellipse yields $r_{22} = \sqrt{(3/32)}c^{\alpha\text{-Zr}}$. Thus, both the major and minor axes of $\alpha\text{-Zr}$ atoms are a sub-multiple of lattice parameters $a^{\alpha\text{-Zr}}$ and $c^{\alpha\text{-Zr}}$, respectively; hence their variations with temperature are similar to the temperature dependence of the corresponding lattice parameters. Since both the isotopic forms of hydrides, i.e. $\delta\text{-ZrH}_x$ and $\delta\text{-ZrD}_x$ have fcc structure with Zr atoms occupying cube corners and face centers and hydrogen or deuterium atoms occupying tetrahedral interstitial sites [7,18,19], Zr-atoms can be thought to be of spherical shape with covalent radius, $r = (\sqrt{2}/4)a^\delta$, where a^δ is the lattice parameter of hydrides or deuterides represented by Eqs. (3) and (4), respectively. At all the applicable temperatures and composition the atomic radius of Zr-atoms, r , in $\delta\text{-ZrD}_x$ phase is marginally smaller than that in $\delta\text{-ZrH}_x$ phase, but shows nearly an identical temperature dependence [16].

4. Atomic volume

The atomic volume of Zr in $\alpha\text{-Zr}$ phase is $\Omega^{\alpha\text{-Zr}} = 4/3\pi(r_{11})^2r_{22}$, where r_{11} and r_{22} are semi-major and semi-minor axes of ellipsoidal Zr atoms defined in Section 3. The atomic volume of Zr in hydride phase is $\Omega = 4/3\pi r^3$, where r is the radius of Zr-atoms as defined in Section 3. The variation in atomic volume of Zr-atoms with temperature in $\alpha\text{-Zr}$, $\delta\text{-ZrH}_x$ and $\delta\text{-ZrD}_x$ is shown in Fig. 3. In general the atomic volume of Zr shows a stronger temperature dependence in hydride phase for both the

isotopic forms as compared to that in $\alpha\text{-Zr}$ phase as is evident from Fig. 3. It may be noted in Fig. 3 that in the temperature range of 298–773 K, atomic volume for $\alpha\text{-Zr}$, $\delta\text{-ZrH}_x$ and $\delta\text{-ZrD}_x$ shows linear temperature dependence. Another feature to be noted is that the difference between the atomic volume of Zr in hydride phase and deuteride phase increases with increase in temperature and hydrogen concentrations.

5. Misfit strain

Since hydrogen or deuterium is present in interstitial site [7,18,19], it was argued by Carpenter [13] that misfit strains, which is also referred to as the stress-free transformation strain, can be computed by considering the change in shape and size of Zr-atoms as a result of phase transformation. Using the atomic radii definition presented in Section 3, the in-basal plane misfit strain is given by $e_{11} = ((r^\delta - r_{11}^\alpha)/r_{11}^\alpha)$ and misfit strain normal to basal plane is given by $e_{22} = ((r^\delta - r_{22}^\alpha)/r_{22}^\alpha)$. Since the close packed planes of $\alpha\text{-Zr}$, $\delta\text{-ZrH}_x$ and $\delta\text{-ZrD}_x$ are parallel with orientation relationship of $(1\ 1\ 1)_\delta \parallel (0\ 0\ 0)_\alpha$ [13], e_{11} is the misfit strain along the hydride platelet and e_{22} is the misfit strain normal to the hydride platelet [13]. The variation in these misfit strains for $\delta\text{-ZrH}_x$ and $\delta\text{-ZrD}_x$ phases for $x = 1.66$ with temperature are represented by Eqs. (5)–(8), with superscripts H and D indicating the hydride and deuteride phase, respectively.

$$e_{11}^H = 0.03888 + 2.315 \times 10^{-5}T \quad (5)$$

$$e_{22}^H = 0.06646 + 1.9348 \times 10^{-5}T \quad (6)$$

$$e_{11}^D = 0.0371 + 2.3111 \times 10^{-5}T \quad (7)$$

$$e_{22}^D = 0.06463 + 1.9315 \times 10^{-5}T \quad (8)$$

For $\delta\text{-ZrH}_{1.66}$ the misfit strain along the hydride platelet, e_{11} , increases from 4.58% at 298 K to 5.21% at 573 K and the misfit strain normal to hydride platelet, e_{22} , increases from 7.22% at 298 K to 7.76% at 573 K. For $\delta\text{-ZrD}_{1.66}$ the misfit strain along the hydride platelet, e_{11} , increases from 4.44% at 298 K to 5.03% at 573 K and the misfit strain normal to hydride platelet, e_{22} , increases from 7.04% at 298 K to 7.57% at 573 K. As is evident from Fig. 4, the misfit strains increases with an increase in temperature and at all the appropriate temperatures the misfit strain for hydride is larger compared to that for deuteride phase. Also, the in-basal plane misfit strain, e_{11} (Fig. 4a), shows a stronger temperature dependence as compared to the misfit strain normal to hydride plate, e_{22} (Fig. 4b), for both hydride and deuteride phases.

The volumetric strain, defined as $\eta = (\Omega_\delta - \Omega_\alpha)/\Omega_\alpha$, where Ω is the atomic volume and the subscripts denote the phase, was also determined for the hydride and deuteride phase. The variation in volumetric strains of $\delta\text{-ZrH}_x$ and $\delta\text{-ZrD}_x$ phases for $1.5 \leq x \leq 1.7$ is depicted in Fig. 5 and is represented by Eqs. (9) and (10), for the generally accepted composition of $\delta\text{-ZrH}_x$ and $\delta\text{-ZrD}_x$ phases for $x = 1.66$, respectively. The volumetric misfit strain for $\delta\text{-ZrH}_{1.66}$ increases from 17.26% at 298 K to 19.29% at 573 K and the corresponding value for $\delta\text{-ZrD}_{1.66}$ are 16.66% and 18.67%, respectively. These differences in the volumetric

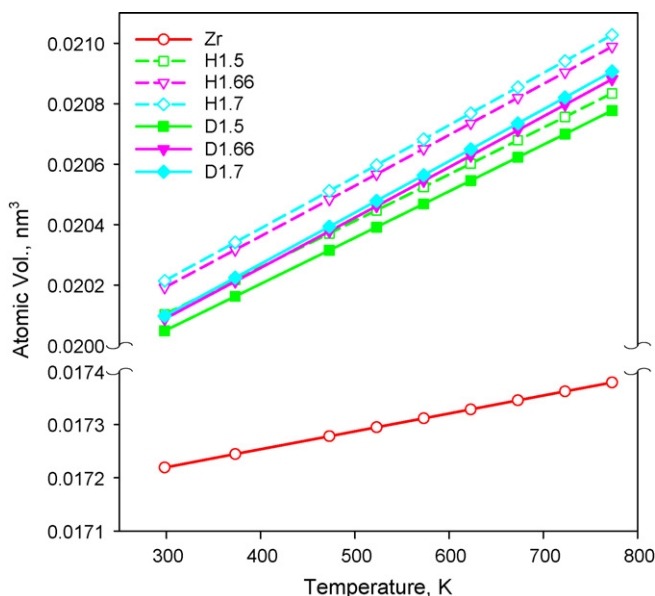
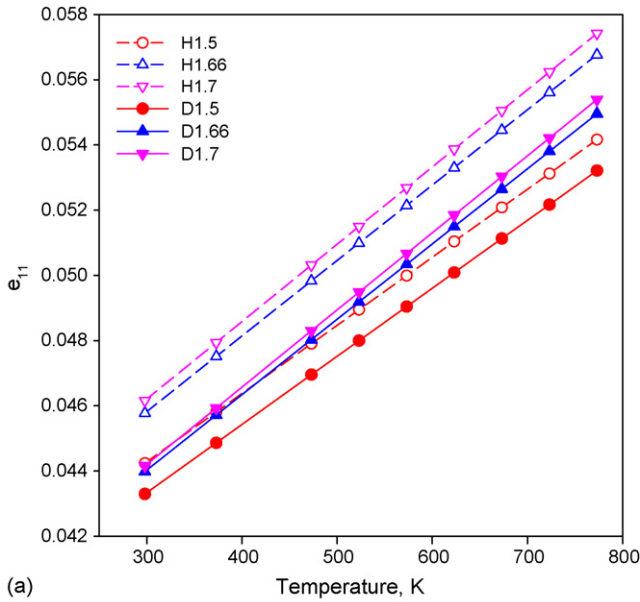
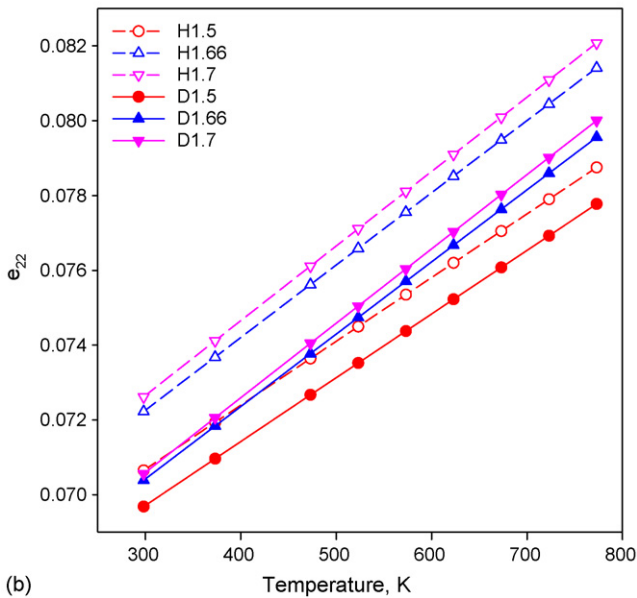


Fig. 3. Variation in atomic volume of Zr-atoms with temperature in $\alpha\text{-Zr}$, $\delta\text{-ZrH}_x$ and $\delta\text{-ZrD}_x$ (for $1.5 \leq x \leq 1.7$).



(a)



(b)

Fig. 4. Variation in (a) in-plane misfit strain, e_{11} , and (b) misfit strain normal to hydride plate, e_{22} , with temperature for both hydride and deuteride phases.

strain for the formation of hydride and deuteride phase can have significant influence on the accommodation energy as the latter is a function of square of the misfit strain [4–6].

$$\eta^H = 0.1506 + 7.38 \times 10^{-5}T \quad (9)$$

$$\eta^D = 0.14469 + 7.3422 \times 10^{-5}T \quad (10)$$

6. Limitations

It may be noted that the computation of misfit strains in Section 5 were based on the lattice parameters of the α -Zr [11,14], δ -ZrH $_x$ [15] and δ -ZrD $_x$ [16] reported in literature. There could be two sources of uncertainty in the values of lattice parameters reported in literature, viz., systematic error due to equipment

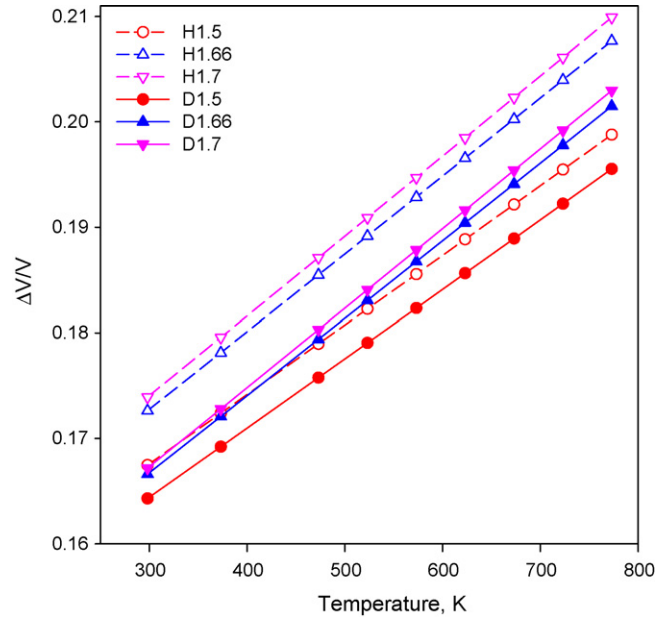


Fig. 5. Variation in volumetric strain, η , with temperature for both hydride and deuteride phases.

used and method of data analysis and due to compositional variation of the samples, which can influence the misfit strains reported in the present investigation. The compositional variation could be either due to the variation in the purity of the Zr samples used for lattice parameter measurement or due to the variation in composition of Zr metal used for preparing hydrides, which are subsequently used for lattice parameter measurement of hydrides. For example, Goldak et al. [20] reported lattice parameter values of $a^{\alpha\text{-Zr}} = 0.32331$ nm and $c^{\alpha\text{-Zr}} = 0.51489$ nm at 298 K compared to $a^{\alpha\text{-Zr}} = 0.3231$ nm and $c^{\alpha\text{-Zr}} = 0.51489$ nm reported by Lloyd [14] and Lichter [11]. Also, the hydride and deuteride samples were prepared from 99.9% pure Zr [15,16].

Dilute Zr alloys used in nuclear industry contains significant amount of oxygen, which is reported to increase both the lattice parameters $a^{\alpha\text{-Zr}}$ and $c^{\alpha\text{-Zr}}$ of Zr metal [11]. On the other hand, Niobium addition to Zr is reported to reduce both the lattice parameters with virtually no change in axial ratio [21] up to niobium content of 1 wt.%. Also, dissolved hydrogen in Zr is reported to increase the lattice parameters [22,23] linearly in the temperature range of 613–833 K. However, the inadequacy of lattice parameter data reported in literature precludes us from making any systematic assessment of dependence of misfit strains due to compositional variation. Assuming that the impurity elements and alloying additions influence the lattice parameters of both α -Zr and hydrides to the same extent, it is felt that the values reported in the present investigation provides a reasonable estimate of misfit strains and its temperature dependence for dilute Zr alloys.

7. Conclusions

The temperature dependence of atomic radii and atomic volume of Zr atoms in α -Zr, δ -ZrH $_x$ and δ -ZrD $_x$ were computed for $1.5 \leq x \leq 1.7$. Using the atomic radii and atomic volume data,

the linear and volumetric misfit strains associated with the formation of hydride and deuteride with respect to α -Zr phase were determined in the temperature range of 298–773 K, which was observed to increase with increase in temperature. The volumetric misfit strain for δ -ZrH_{1.66} and δ -ZrD_{1.66} increased from 17.26 and 16.66%, respectively, at 298 K to 19.29 and 18.67%, respectively, at 573 K. Both linear and volumetric misfit strains for deuteride phase were marginally lower than that for hydride phase.

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