Mean-field Strain in Zirconium Hydride

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Abstract

The formation of hydrides in zirconium alloys will cause degradation of the materials. Despite extensive study, the mechanisms and effects of hydrogen embrittlement have remained unclear. In this report, we had presented the calculation results of mean-field strain by different hydride phases in zirconium alloys, like δ-hydride and γ-hydride. The results of δ-hydride are compared with experimental data obtained by X-ray diffraction method by Bai et al.[1] and note [2] of Massih. The result of δ-hydride is identical with Massih but have some differences with Bai et al. We had also compared our calculated mean-field strain by γ-hydride with δ-hydride. The γ-hydride showed lower value than δ.

Keywords: Zirconium alloy, Zircaloy, Mean-field strain, δ-hydride, γ-hydride, Mori-Tanaka model

1 Introduction

Zirconium alloys are widely used in the nuclear industry as fuel rod cladding material because of their excellent mechanical properties, low neutron absorbability and high corrosion resistance. However, similar to other hydride forming metals zirconium alloys have a serious drawbacks, known as "hydrogen embrittlement". At low temperature hydrogen has a very low terminal solid solubility (TSS) in hexagonal close packed α-zirconium phase, any further hydrogen uptakes after TSS will lead to precipitation of brittle hydride phase and degrade the performance of the material [3, 4, 5, 6, 7]. The degradation of material properties depends on the concentration, distribution and morphology of the hydrides. The detrimental effect of hydride rich maximum when they are oriented normal to applied load (radial hydrides in the case of tubes under internal pressure)[8]. Thus, there is a need to understand the affect of hydride faces in zirconium alloys, yet there are many things still unclear. So for the purpose of better understanding and fill the small parts of the gap, we have made the presented here.

The equilibrium phase diagram of zirconium-hydrogen (Zr-H) system was quite complex and hard to study, since formation of different hydride

phases is dependent on hydrogen concentration and cooling rate [5, 9]. However, Zr-H system has been examined by many studies, and was reported that: it includes two allotropic forms of zirconium, hexagonal close packed (hcp) α-Zr and body centered cubic (bcc) β-Zr; two other stable hydride phases, face centered cubic (fcc) δ-hydride and face centered tetragonal (fct) ϵ-hydride, and one metastable fct γ-hydride which can exist at the lower temperatures in $\alpha - \beta - \delta$- phase region [10, 9, 11].

In this report, we first present the results from recalculation of data for δ-hydrides in Zircaloy given by Bai et al.[1]. Thereafter we show the mean-field strain on zirconium matrix by γ-hydride. This work was initiated by professor Ali R. Massih. During Massih's research he found that there are few wary data in reference [1], and he suggested to recalculate the results in [1]. Based on this, we had started our work with reproducing Bai et al.'s calculations related to the mean-field strain by δ-hydride. Then, we had compared our calculations with both Bai et al. and Massih [2]. In the end, we also had showed calculated mean strain by γ-hydride with the same model, and comparison with γ-hydride.

2   The work of Bai et al.

Bai et al. used the transmission electron microscopy (TEM) and the X-ray diffraction technique (XRD) to estimate the dislocation density, and correlation of hydride morphology with strains, respectively. The characteristic parameters, which they studied, are the coherent domain size D and distortion factor ϵ_1. D is the size in a given crystallographic direction of a 3D perfect crystal domain and is limited by crystallographic defects in the specimen. ϵ_1 is an image of the distortion in a given direction induced by the defects around the coherent domains. Bai et al. defined the micro-strain as

$$< \epsilon_L{}^2 >= \frac{\epsilon_1}{L}, \tag{1}$$

where L is a characteristic length of cell columns in a sample that is taken to be 100 in this case. Based on these parameters Bai et al. calculated the average dislocation density $< \rho >$ according to the formula:

$$< \rho >= c \frac{< \epsilon_L{}^2 >^{\frac{1}{2}}}{D \mid \overrightarrow{b} \mid}, \tag{2}$$

where c is a dislocation constant equal to 12 for Zircaloy, and $\overrightarrow{b}$ is the Burger's vector. According to Equ.2, the mean-field strain is proportional to Burger's vector, but dislocation density is not. Through TEM observation, Bai et al. found that the all hydrides in Zircaloy-4 under slow cooling rate were fcc δ-hydride. At 350 wppm hydrogen, both intra- and intergranular

Table 1: Essential data from Bai et al.'s experiment [1] and related calculation results

Source	H content(wppm)	5	350	660	760	1248
Bai et al.	D (Å)	1479.0	709.0	545.0	534.0	476.0
	$\epsilon_1(\times 10^{-6})$	17.0	52.0	76.0	78.0	86.0
	$\rho(\times 10^{10} cm^{-2})$	1.37	5.97	10.10	10.50	13.27
	$< \epsilon_L{}^2 >^{\frac{1}{2}} (\times 10^{-4})$		7.2	8.7	8.8	9.3
Author		4.123	7.211	8.718	8.832	9.274
	$\mid \overrightarrow{b} \mid (\times 10^{-10} m)$	2.442	2.044	1.901	1.89	1.762

hydride platelets were observed. In nonhydrided specimens, the dislocation structure was composed of straight dislocation lines with the density of 1-$2 \times 10^9 cm^{-2}$. In contrast, in hydrided specimen (hydrogen content>5 wppm) a tangled dislocation network was observed around δ-hydrides with average dislocation density of $1.1 \times 10^{10} cm^{-2}$ [1].

The data from Bai et al.'s experiment that we have used in our study is given in Table 1. Since Bai et al. did not give the value of Burger's vector, we first calculated it from Equ.(1) and (2) to check whether experimental values are reasonable or not.

3   Mean-field strain

The internal stresses of an inclusion and on its interface can be calculate by Eshelby's theory [12]. In the case of transformation misfit stress or strain in matrix formed by the inclusions can be evaluate by Mori-Tanaka's model [13].This model was based on Eshelby's theory. In this model, the mean-field strain in the matrix is expressed as:

$$\widetilde{\epsilon}_{ij} = V_f(\epsilon_{ij}{}^T - S_{ijkl}\epsilon_{kl}^T), \tag{3}$$

where $\epsilon_{ij}{}^T$ is the transformation or stress-free misfit strains caused by stress-free deformation of hydrides; V_f is the hydride volume fraction and can be derived from Equ.(9) in [8]:

$$C_{HT} = (\frac{x}{91 + xV_f})(10^6)V_f, \tag{4}$$

where x is the hydride composition index (ZrH_x), C_{HT} is the hydrogen concentration. S_{ijkl} in equation (3) is the Eshelby tensor, which is a function of configuration such as orientation and shape of the hydride (inclusion). The components of S_{ijkl} for a specific shape, like plates, needles and spheres, are functions of Poisson's ratio, ν, are given by [2],[14] and [15].The calculated Eshelby tensor components with ν=0.37 for three different shapes are presented in Table 2.

Table 2: The components of the Eshelby tensor

Type	Source	Eshelby tensors					
		S_{2211}	S_{2222}	S_{2233}	S_{3311}	S_{3322}	S_{3333}
δ	Bai et al.	0.009	0.045	0.005	0.543	0.543	0.991
	Massih	0.0087	0.0447	-0.0046	0.5431	0.5431	0.991
		0.0087	0.0447	-0.0046	0.543	0.543	0.991
γ	Author	0.095	0.698	0.294	0	0	0
Spherical		0.0899	0.545	0.089	0.089	0.089	0.545

Figure 1: Habit planes of $\alpha-$Zr and $\gamma-$ zirconium hydrides:a) crystallographic planes and directions of hexagonal $\alpha-$Zr crystal; b) $\gamma-$hydride needle lying along $[11\bar{2}0]$ [17][2].

The transformation strains have been evaluated by Carpenter [16]. In δ-hydride, two hydride orientations are considered: a plate lying on the basal plane [0001] and a plate lying on the prism plane $[1\bar{1}00]$ of the hexagonal α-Zr crystal (Fig.1.a).

From Table 2 , we can see that there are sign differences between Bai et al. and ours on S_{2233}, but it is same with Massih. Since the magnitude is similar, we think it might be a typing mistake.

With a random distribution of plate-like hydrides, the tensorial relation (3) can be written as

$$\widetilde{\epsilon}_{33} = \frac{V_f}{3}[(2\epsilon_{22}{}^T + \epsilon_{33}{}^T) - 2(S_{2211}\epsilon_{11}^T + S_{2222}\epsilon_{22}^T + S_{2233}\epsilon_{33}^T)$$
$$-(S_{3311}\epsilon_{11}^T) + S_{3322}\epsilon_{22}^T) + S_{3333}\epsilon_{33}^T))] \qquad (5)$$

if we substitute the value of $[\epsilon_{11}^T, \epsilon_{22}^T, \epsilon_{33}^T] = [0.0458, 0.0458, 0.072]$ [16] and components of Eshelby tensor which presented in Table 2, we will have

$$\widetilde{\epsilon}_{33} = 0.012763V_f \qquad (6)$$

Our results is identical with results of Massih ($\widetilde{\epsilon}_{33} = 0.012764V_f$), but 3% differs from Bai et al.'s calculation ($\widetilde{\epsilon}_{33} = 0.012406V_f$) by approximately. Even we have such close expression for $\widetilde{\epsilon}_{33}$, we could not obtain similar results after substitute hydride volume fraction (V_f) both published in [1] and our calculated value. So, we had calculated $\widetilde{\epsilon}_{33}$ with Bai et al.'s data to cross check. However, both Equ.[A9]

$$\widetilde{\epsilon}_{33} = \frac{V_f}{3}[(2\epsilon_{11}{}^T + \epsilon_{33}{}^T) - 2(S_{2211}\epsilon_{11}^T + S_{2222}\epsilon_{22}^T + S_{2233}\epsilon_{33}^T)$$
$$-(S_{3311}\epsilon_{11}^T) + S_{3322}\epsilon_{22}^T) + S_{3333}\epsilon_{33}^T))]$$

Table 3: The mean-field strain and volume fraction of δ-hydride

Source	Parameter	Data				
	H content(wppm)	5	350	660	760	1248
Bai et al.[1]	$V_f(\times 10^{-2})$	0.03	1.95	3.68	4.24	6.97
Author		0.028	1.93	3.64	4.19	6.89
Bai et al. [1]	$\widetilde{e}_{33}(\times 10^{-4})$		6.5	8.7	9.4	12.8
Bai et al.[1]should be		0.039	2.37	4.47	5.15	8.46
Massih [2]		0.038	2.49	4.70	5.41	8.89
Author		0.035	2.46	4.65	5.35	8.796

Figure 2: Comparison of mean-field strain by δ-hydride

and Equ.[A10]

$$\widetilde{\epsilon}_{33} = V_f \frac{2}{3}\epsilon_{11}^T(1 - S_{3311})$$

in [1] did not give the either published nor our calculated values ([A9]→ 0.012281V_f, [A10]→ 0.013954V_f). In Equ.[A9] there is a printing mistake in indices of first strain term, but for δ-hydride the $\epsilon_{11}^T = \epsilon_{22}^T$. So it is not clear for us why Bai et al. have about 5% higher value than us and Massih. Bai et al. ignore the mean-field strain in specimen with 5 wppm hydrogen concentration in Table 5 and Fig.5 in [1], but from their presented data in Table 4 we got it is not zero (4.123×10^{-4}). The value of $\widetilde{\epsilon}_{33}$ by different source and model-fit are shown in Table 3 and graphically illustrated on Fig.2. The experimental XRD measurements by Bai et al. was expressed as $< \epsilon_L{}^2 >^{\frac{1}{2}}$ in current paper and as well as [1].

4   γ-hydride

Even there are wide range of study undertaken about zirconium-hydride, still the nature of γ-phase (ZrH) is unclear and controversy exist about its stability [18, 19]. The γ-phase has an ordered tetragonal unit cell with lattice parameters a=b=0.4586 nm, c=0.4948 nm and vol.=104.06 $\mathring{A}^3$, where the hydrogen atoms on the tetrahedral sites of the (110) plane. The γ-hydride is considered to be a needle-like precipitate, and can be approximated by a long ellipsoid. The transformation from a single crystalline hexagonal zirconium to tetragonal γ-hydride produces three possible orientation variants(Fig.7.b).The eigenstrains for the first orientation parallel to [11$\bar{2}$0] are given as

Table 4: The average mean-field strain and volume fraction of γ-hydride

Source	Parameter	Data				
	Hydrogen content(wppm)	5	350	660	760	1248
Author	V_f (%) ZrH	0.046	3.19	6.01	6.92	11.37
	$\widetilde{\epsilon}_{33}$ ($\times 10^{-4}$)	0.024	1.67	3.15	3.63	5.97

Figure 3: Comparison of mean$-$field strain by different hydride versus hydrogen concentration

$$\epsilon_{ij}^{\mathbf{T}} = \begin{pmatrix} 0.057 & 0 & 0 \\ 0 & 0.00551 & 0 \\ 0 & 0 & 0.0564 \end{pmatrix} \qquad (7)$$

[16].The other two sets of eigenstrains can be obtained by rotation of (7) through 120° and 240°, about the z-axis of hexagonal close packed structure, respectively [2][20].

From tensor algebra the transformation can be written as

$$\epsilon_{ij}^{'} = a_{mi}a_{nj}\epsilon_{mn}, \qquad (8)$$

where a_{kl} is the transformation matrix. Since this transformation is a simple calculation, we will not present it here. The Eshelby tensor components (S_{ijkl}) for needle-like inclusion was formulated by Brown et al.[15]. The value of S_{ijkl} are listed in Table 2.

Based on equation (5), which we used to calculate the mean-field strain by δ-hydride, we can calculate the mean-field strain in [11$\bar{2}$0] direction by γ-hydride. The calculated volume fraction and average mean-field strain by γ-hydride are shown in Table 4. For see the effect of different shapes on strain, we will draw: strain versus hydride content, this curve shown in Fig.3.

5   Spherical hydride

Sphere is a hypothetical shape for hydrides, and it is not common to have such hydride in real world. However, it can be used for analytical evaluations and model validation. On the other hand, in the beginning of nucleation, hydride can be assumed as spherical and later it would reshape into a plate- or a needle-like precipitate [2]. The fourth rank of Eshelby tensor is expressed as[14]

$$S_{ijkl} = \frac{5\upsilon - 1}{15(1-\upsilon)}\delta_{ij}\delta_{kl} + \frac{4-5\upsilon}{15(1-\upsilon)}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \qquad (9)$$

where δ_{mn} is stands for kronecker delta, ν is Poisson's ration which is equal to 0.37 for this case. For simplicity, we calculate S_{ijkl} in three different indices state:

$$S_{iiii} = \frac{7 - 5\nu}{15(1 - \nu)}, S_{iijj} = \frac{5\nu - 1}{15(1 - \nu)}, S_{ijij} = \frac{4 - 5\nu}{15(1 - \nu)}$$

the calculated value was presented in Table 2.

Acknowledgement

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