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锆合金中氢化物应力再取向的研究

A STUDY OF STRESS REORIENTATION OF HYDRIDES IN ZIRCALOY

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摘　要

渗氢后，氢含量约为 220 μg/g 左右的 Zr-4、Zr-2 管和 Zr-4 板，在周向张应力为 70～180 MPa（Zr 管）或张应力为 55～180 MPa（Zr-4 板）作用下，在 150～400℃温度区间进行循环。研究了应力和温度循环次数对氢化物再取向程度的影响。随着应力增大和温度循环次数增加，氢化物再取向程度也增大，但是氢化物发生再取向存在应力阈值。应力阈值与温度循环次数有关，当张应力低于应力阈值时，氢化物应力再取向不明显；当应力大于应力阈值时，氢化物应力再取向程度随着与应力、温度循环次数增加而增大。Zr-4 管中氢化物发生再取向时，首先从管壁外表面开始，逐渐向内推进，这可能与内、外表面织构不同有关。织构不仅对应力阈值有影响，而且也影响 *B* 值，因此控制织构仍可以制约氢化物发生应力再取向。

A STUDY OF STRESS REORIENTATION OF HYDRIDES IN ZIRCALOY

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ABSTRACT

Under the conditions of circumferential tensile stress from 70 to 180 MPa for Zircaloy tubes or the tensile stress from 55 to 180 MPa for Zircaloy-4 plates and temperature cycling between 150 and 400℃, the effects of stress and the number of temperature cycling on hydride reorientation in Zircaloy-4 tubes and plates and Zircaloy-2 tubes containing about 220 μg/g hydrogen have been investigated. With the increase of stress and/or the number of temperature cycling, the level of hydride reorientation increases. When hydride reorientation takes place, there is a threshold stress concerned with the number of temperature cycling. Below the threshold stress, hydride reorientation is not obvious. When applied stress is higher than the threshold stress, the level of hydride reorientation increases with the increase of stress and the number of temperature cycling. Hydride reorientation in Zircaloy-4 tubes develops gradually from the outer surface to inner surface. It might be related to the difference of texture between outer surface and inner surface. The threshold stress is affected by both the texture and the value of B. So controlling texture could still restrict hydride reorientation under tensile stress.

INTRODUCTION

In nuclear reactor Zircaloys have been used for fuel cladding in contact with hot water or steam, and the cladding absorbs some of hydrogen produced by the cladding corrosion during the reactor operation. The presence of hydrogen in excess of terminal solubility can result in severe embrittlement due to the precipitation of zirconium hydrides, especially in the radial direction. Hydride orientation could be controlled by texture because there is a habit plane during the hydride precipitating, but hydride reorientation perpendicular to tensile stress could take place. This is a matter of greater concern because of the presence of stress in the fuel cladding and grid spacer of Zircaloy-4 plate due to different texture and texture coefficient in different direction during the latter stage of reactor operation. It will become more important with the increase of discharge burn-up. So it is necessary to investigate the effects of stress and the number of temperature cycling on reorientation of hydride in Zircaloy, and the experimental results could be referred in the design and operation of nuclear reactors.

1 EXPERIMENTAL PROCEDURE

After being polished chemically in the solution of 10%HF, 45%HNO_3, and 45%H_2O, annealed Zircaloy-2, Zircaloy-4 tubes and Zircaloy-4 plates were autoclaved at 360℃ water containing 1 mol/L LiOH in order to absorb hydrogen about 220 μg/g, which was estimated by comparison with standard atlas[1]. For Zircaloy tubes, under a constant circumferential stress, which of the Zircaloy-4 were measured at room temperature by stress-strain gauge under different loads, produced by vertically pressing down graphite powder fulled in Zircaloy tube. For Zircaloy-4 plates, under different stresses produced by pulling specimen with a taper shape in gauge length, which gave different sizes of section. Under a load temperature cyclings between 150℃ and 400℃ were carried out for hydride reorientation because the range of temperature is roughly equal to that of fuel cladding in nuclear reactor. The terminal solubility of hydrogen in Zircaloy is about 200 μg/g at 400℃, and only about 5 μg/g at 150℃[2]. During temperature cycling the hydrides dissolve and precipitate alternately that can sufficiently show the relationship of hydride reorientation. A parameter, f_{45}, which is the fraction of hydride platelets orientated within 45° to the reference direction, is used to describe the level of hydride reorientation and was measured by image instrument[3] after the specimens were polished and etched. Textures of the experimental materials were measured by X-ray diffraction.

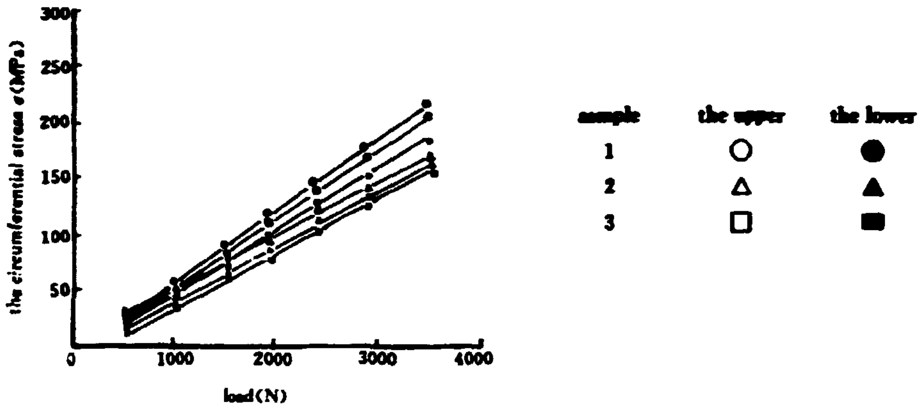


Fig. 1 The relationship between load and the circumferential stress of Zircaloy-4 tube

2 RESULT

2.1 The circumferential stress of Zircaloy tube

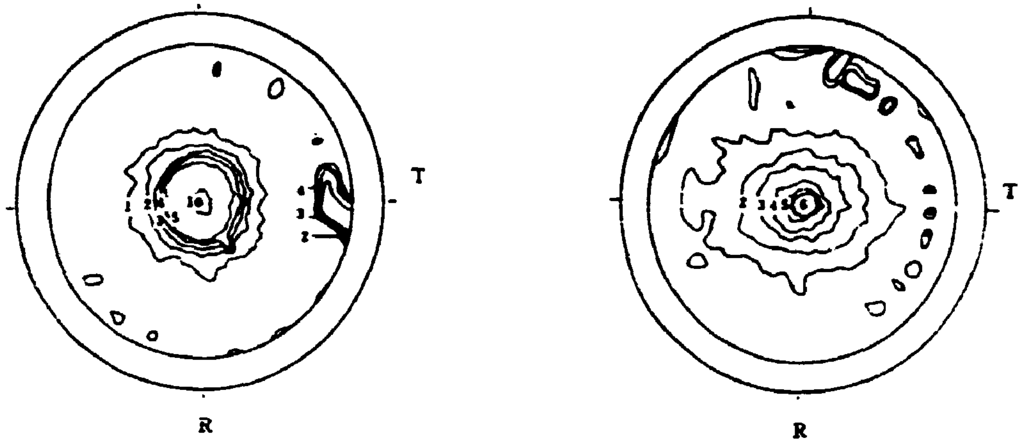
The circumferential stresses of Zircaloy-4 tube under different loads are shown in Fig. 1. The stress at the upper part is higher than that at the lower part of Zircaloy-4 tube, but the difference is not large, the average of stresses under different loads are as the following: (0.627 mm thickness of Zircaloy-4 tube)

load (N)	1500	1900	2500	2900
the stress (MPa)	70	92	125	145

In Zircaloy-2, the relationship between the circumferential stress and load is given as follows:

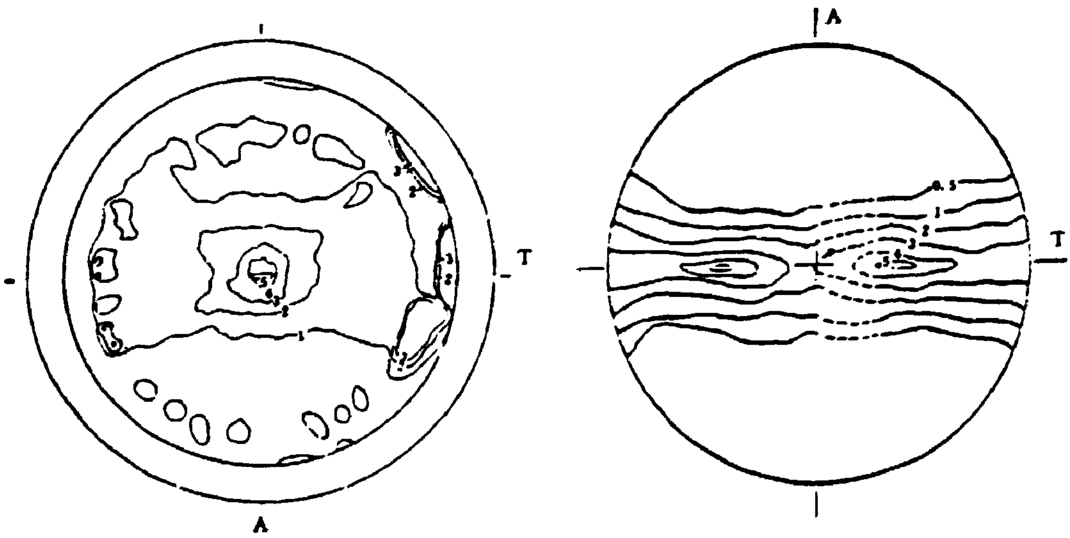
$$\sigma_\theta = 2.815 \times P/(3.14 \times r^2) - 7.14$$

where P (N) is load, r (mm) is radius. The circumferential stress is concerned with load, radius and thickness of tube, but not with elasticity. The stress must be kept a constant under a certain load during temperature cycling between 150℃ and 400℃.



a. Sp···imen with 0.6 mm thickness b. Specimen with 2.3 mm thickness

Fig. 2 The (0002) pole figure of Zircaloy-4 plates



a. Zircaloy-4 tube b. Zircaloy-2 tube[4]

Fig. 3 The (0002) pole figure of Zircaloy-4 and Zircaloy-2 tubes

2.2 Textures of Zircaloy-2, Zircaloy-4 tube and Zircaloy-4 plate

Density of (0002) pole in the direction normal to rolling (RD) in specimen with 0.6 mm thickness is stronger than that in the rolling direction (Fig. 2). Hydrides in the specimen reorientate easily under tensile stress applied normal to the rolling direction. The highest pole density of (0002) in Zircaloy-4 tube locates at the center of (0002) pole figure in Fig. 3. Hydride in the Zircaloy-4 tube orientates in the circumferential direction, and it is not easy for hydride reorientation under the circumferential tensile stress. The highest pole density of (0002) in Zircaloy-2 tube deviates 30° from the center towards transversal direction. i. e, the pole density of tangential direction in the Zircaloy-2 tube is stronger than that in the Zircaloy-4 tube. Hydrides in tube with such texture orientate easily in the radial direction and reorientate under the circumferential stress.

2.3 Effect of stress and temperature cyclings on hydride reorientation in Zircaloy tubes

Hydrides precipitate on certain planes (habit plane) in α-Zr, the habit plane for Zircaloy-2 and Zircaloy-4 is $\{10\bar{1}7\}$. A large volume increase (14%~17%) occurs when α-Zr is transformed into hydride, so hydride precipitates easily in the direction normal to the tensile stress and parallel to the compressive stress, i. e, hydride reorientation takes place under stress.

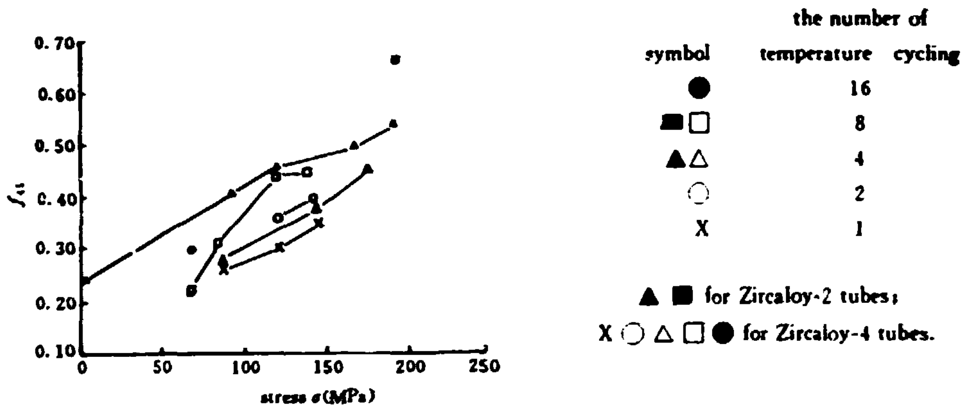


Fig. 4 The relationship among the value of f_{45}, the tensile stress and the number of temperature cycling in Zircaloy tubes

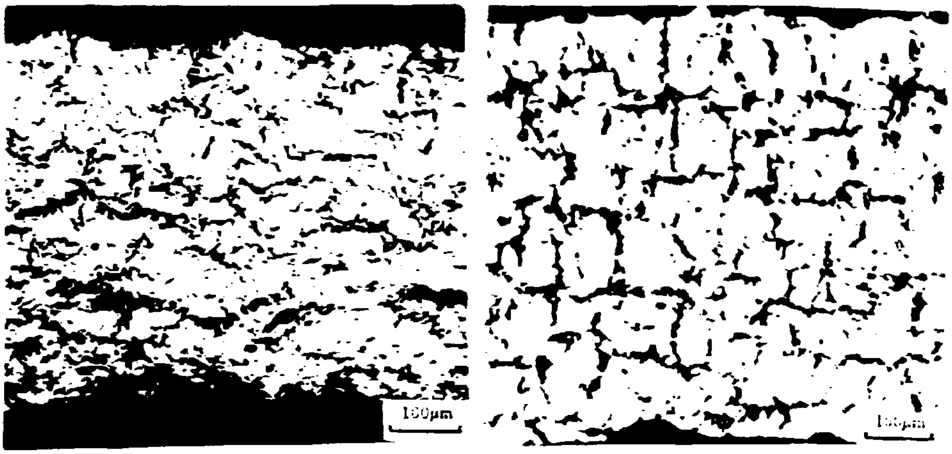
The level of hydride reorientation increases with the increase of stress or the number of temperature cycling (Fig. 4). When the hydride reorientation takes place, there is a threshold stress (σ_{n}') which is concerned with the number of temperature cycling. Under the same stress, hydride reorientation in Zircaloy-2 tube is easier than that in Zircaloy-4 tube due to the different texture.

Hydride parallel to the tensile stress dissolves preferentially with the increase of temperature, and precipitates preferentially in the direction normal to the tensile stress with the decrease of temperature. The presence of hydrides has the promotive effects on hydride nucleation or growth[5,6]. So the level of hydride reorientation increases with the increase of number of temperature cyclings under a certain stress level.

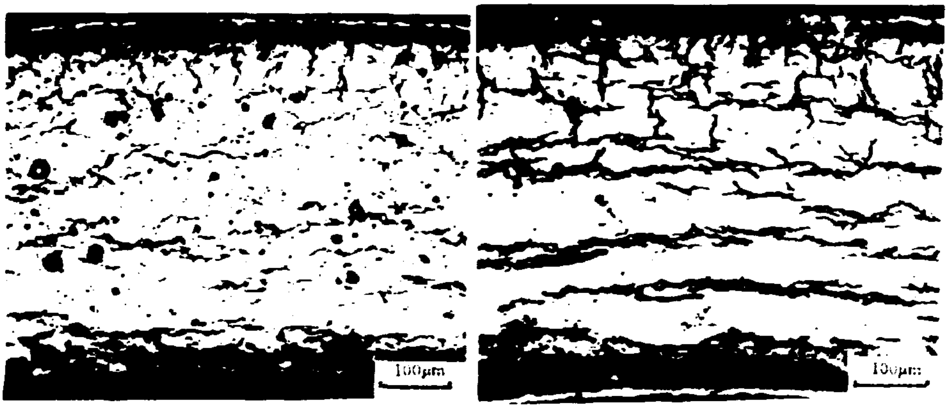
With the same number of temperature cycling, the value of f_{45} increases with tensile stress level, in fact, the number of hydrides precipitating parallelly to the radial direction increases. The value of f_{45} increases with the number of temperature cycling under the same stress. Below the stress level of 70 MPa in Zircaloy-4 tube, hydride reorientation is not obvious even if the number of temperature cycling increases. It illustrates that there is a threshold stress when hydride reorientation takes place.

Hydride distributions in several experimental conditions are shown in Fig. 5. There are a lot of hydrides reorientated to form radial distribution in Zircaloy-2 tube. Hydrides in Zircaloy-4 tube reorientate not simultaneously along the radial direction, it takes place gradually from the outer surface of tube to the inner surface with the increase of stress or the number of temperature cycling, and there is an obvious demarcation between reorientated hydrides and unreorientated ones. This phenomenon has not been reported in literature[7]. Although hydride distribution is affected by many factors[8], the phenomenon might be related to the difference of texture in outer surface and/or the different state of stress. Hydride reorientated in the radial direction at the outer surface has the promotive effects on hydride nucleation in this direction[6]. So hydride reorientation takes place gradually from the outer surface of tube to the inner surface.

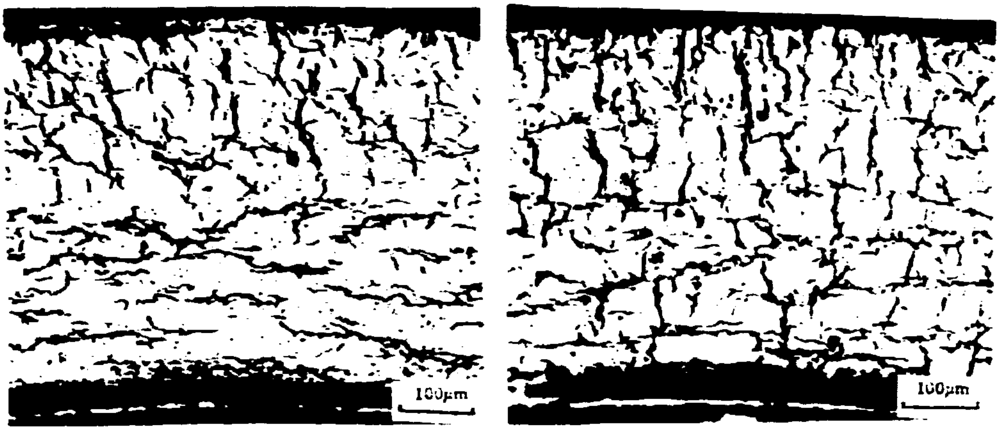
With the increase of stress and the number of temperature cycling, hydride reorientation could take place in whole section of Zircaloy-4 tube, but the value of f_{45} is smaller than 1, only 0.50. This might be related to texture. If the (0002) pole is nearly parallel to the radial direction of tube, it is not easy for hydride to distribute and to reorientate in the radial direction. So controlling texture is still effective on controlling hydride reorientation under stress.



Zircaloy-2 tube autoclaved (a) and after temperature cycling
4 times under the stress of 186 MPa (b)



Zircaloy-4 tube autoclaved (c) and after temperature cycling
2 times under the stress of 96 MPa (d)



Zircaloy-4 tube after temperature cycling 2 times under the stress
of 145 MPa (e) and 8 times under the stress of 146 MPa (f)

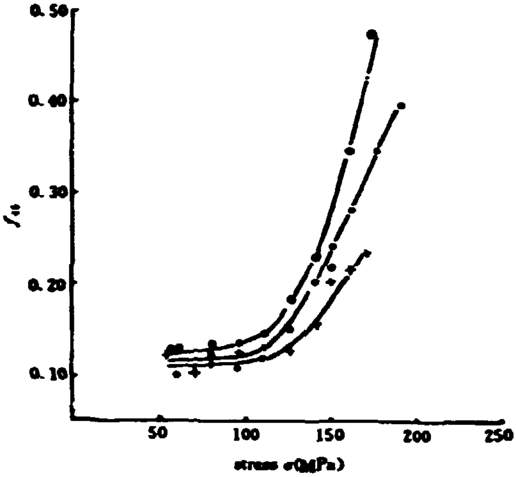
Fig. 5 Distributions of hydrides in Zircaloy tubes at various conditions

2.4 Effect of stress and temperature cyclings on hydride reorientation in Zircaloy-4 plates

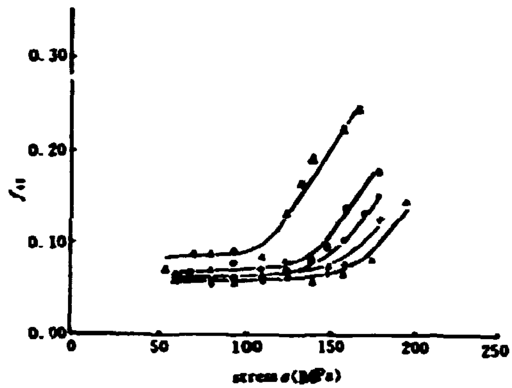
For Zircaloy-4 plates the level of hydride reorientation increases with the increase of stress or the number of temperature cycling (Fig. 6). When hydride reorientation takes place, there is a threshold stress (σ_n) which decreases with increasing the number of temperature cycling. the relationship can be shown empirically as follows:

$$\sigma_n = \sigma_1 \quad (1 - 1/n)C \tag{1}$$

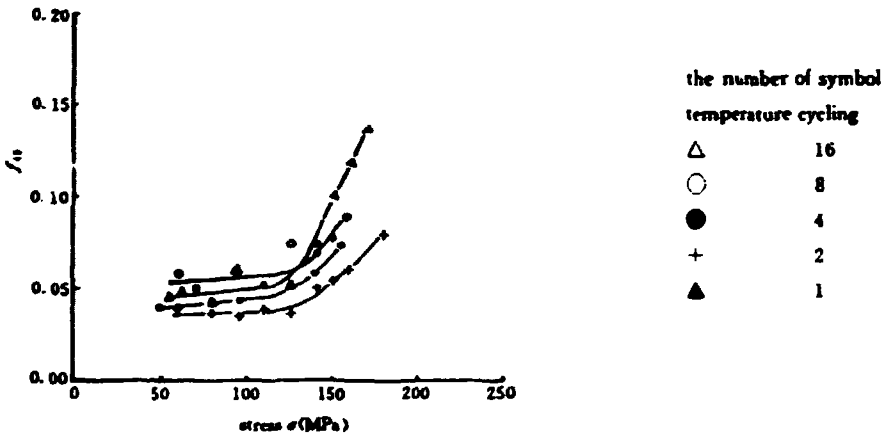
where σ_n (MPa) is a threshold stress with n times temperature cycling. σ_1 (MPa) is a threshold stress when n equals to 1. C is a constant concerned with material characteristics (e. g. texture) and the experimental conditions.



a. Zircaloy-4 plates (0.6 mm thickness) under the tensile stress normal to the rolling direction



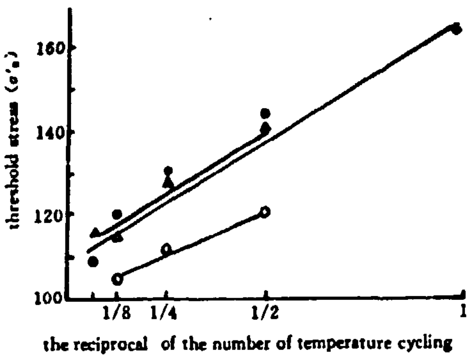
b. Zircaloy-4 plates (0.6 mm thickness) under the tensile stress parallel to the rolling direction



c. Zircaloy-4 plates (2.3 mm thickness) under the tensile stress parallel to the rolling direction

Fig. 6 The relationship among the value of f_{45}, the tensile stress and the number of temperature cycling in Zircaloy-4 plates

In Fig. 7, straight lines intersect with longitudinal coordinate, and the intersection is the threshold stress when n is infinite. For Zircaloy-4 plate (0.6 mm thick), it is 90 MPa and 110 MPa respectively when the tensile stress is normal to and parallel to the rolling direction. For Zircaloy-4 plate (2.3 mm thick), it is 115 MPa when the tensile stress is parallel to the direction. When the applied stress is lower than above-mentioned value, hydride reorientation is not obvious even if the number of temperature cycling increases. When n is a certain constant, the level of hydride reorientation increases rapidly with tensile stress more than the threshold stress (σ_n'). Hydride distributions in different experimental conditions are shown in Fig. 8. There are more hydrides reorientated normally to tensile stress in Zircaloy-4 plate (0.6 mm thickness) with increasing the tensile stress and the number of temperature cycling.

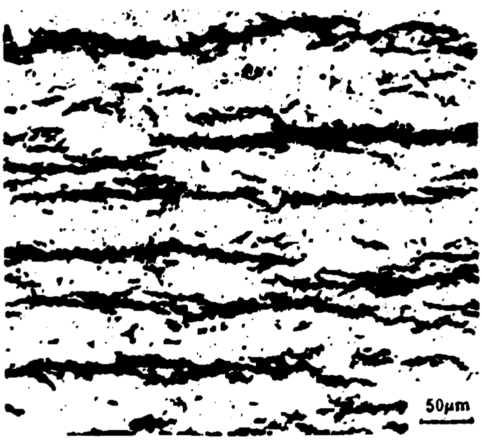


○ 0.6 mm thickness, tensile stress normal to the rolling direction

● 0.6 mm thickness, tensile stress parallel to the rolling direction

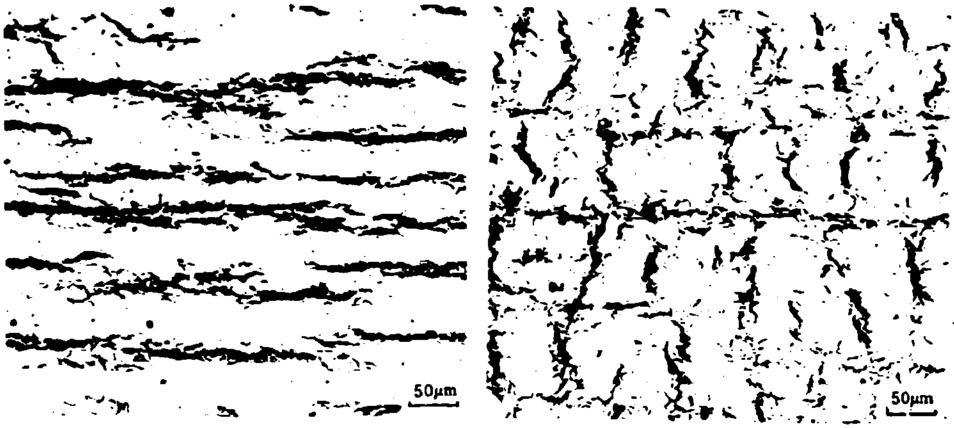
△ 2.3 mm thickness, tensile stress parallel to the rolling direction

Fig. 7 The relationship between the threshold stress of hydride reorientation and the number of temperature cycling in Zircaloy-4 plates



a. temperature cycling 2 times under the stress of 80 MPa

b. temperature cycling 2 times under the stress of 168 MPa



c. temperature cycling 8 times under the stress of 80 MPa

d. temperature cycling 8 times under the stress of 156 MPa

The direction of applied stess →

Fig. 8 Distributions of hydrides in Zircaloy-4 plate at different conditions under tensile stress normal to the rolling direction

3 DISCUSSION

Ells[9] used the stress orientating mechanism of the precipitation of $Fe_{16}N_2$ in iron derived by J. C. M. Li, and obtained the relationship between the level of hydride reorientation and tensile stress:

$$R_\sigma = R_0 \exp[B\sigma] \tag{2}$$

where R_0 and R_σ are the level of hydride orientation in the original state and hydride reorientation under stress respectively, $R = f_\theta/(1 - f_\theta)$, B is a constant related to material. Marshall[10] and Louthan's[11] data were explained with Eq. (2), Hardie's[12] data satisfied Eq. (2) too. But Eq. (2) does not include a threshold stress which does exsist during hydride reorientation as showing both in our experimental data and Stehle's[13] data. According to the data obtained in present work, the relationship among the level of hydride reorientation, the number of temperature cycling and the threshold stress is given empirically as follows:

$$R_\sigma = R_0 \exp[B n^{\frac{1}{3}}(\sigma - \sigma_n')] \tag{3}$$

where B is a constant concerned with material and experimental conditions. The Eq. (3) is true under the prerequiste conditions: applied stress must be between σ_n' and $\sigma_{0.2}$ ($\sigma_{0.2}$ means yield strength at the highest temperature during temperature cycling) and most of hydrides dissolve at the highest temperature and precipitate at the lowest temperature. Our experimental and Stehle's data were fitted respectively with Eq. (2) and (3) (Table 1 and 2). From Table 2 it is seen that deviations of B are very small which correspond to definiting B as a constant. Interrelation coefficients are large. Deviations of f_{45} are small and calculated threshold stresses are correspond to ones measured from the experimental curves (in the range of experimental error[13]). So Eq. (3) is better to describe the relationship among hydride reorientation, tensile stress and the number of temperature cycling.

B and threshold stress (σ_n') are two important parameters to describe the level of hydride reorientation. Because hydrides in Zircaloy-4 almost precipitate on $(10\bar{1}7)$habit plane, if the smaller is the angle between tensile stress and the pole of (0002), the easier develops hydride reorientation and the lower is the threshold. the difficulty of hydride reorientation has close relationship with the direction of tensile stress and pole of (0002), Threshold stress with tensile stress parrallel to the rolling direction is lower and the value of B is higher than that with tensile stress normal to it, because coefficient of texture is different in the direction of tensile stress. Hardie reported that hydride distrubition before reorientation only affected on the threshold stress, did not on the value of B. Our results show that the larger the value of R_0 is, the larger the value of B is.

Table. 1 Result of fitting the experimental data according to $R_r = R_0 \exp[B\sigma]$

Serial number of sample	Direction of applied stress	The number of temperature cycling	R_0	$B\times10^{-3}$	Interrelation coefficient of $\ln R_r - \sigma$	Deviation of f_{45}
32		2	0.1308	7.23	0.8808	0.0211
36	normal to	4	0.1113	14.47	0.9562	0.0298
33	RD*	8	0.1510	12.85	0.8518	0.0537
45		1	0.0697	4.12	0.5575	0.0177
40		2	0.0635	4.83	0.7984	0.0110
43	parallel to	4	0.0585	9.14	0.9290	0.0128
46	RD*	8	0.0656	10.52	0.9147	0.0150
41		16	0.1021	13.71	0.9301	0.0267
56		2	0.0455	7.60	0.7261	0.0134
51	parallel to	4	0.0434	10.16	0.8479	0.0146
55	RD**	8	0.0567	3.98	0.7762	0.0075
58		16	0.0468	9.60	0.8728	0.0149
Ref. [13]			0.1765	19.15	0.8384	0.5433

note: * Zircaloy-4 (0.6 mm thickness), ** Zircaloy-4 (2.3 mm thickness)

Table. 2 Result of fitting the experimental data according to $R_s = R_0 \exp[Bn^{1/3}(\sigma - \sigma_n')]$

Serial number of sample	Direction of applied stress	The number of temperature cycling	R_0	$B \times 10^{-3}$		Interrelation coefficient of $\ln R_s - \sigma$	Deviation of f_{45}	Threshold stress σ_n'(MPa)
				B	Deviation			
32	normal to RD*	2	0.1308	12.80	0.14	0.9601	0.0134	123
36		4	0.1113			0.9980	0.0066	114
33		8	0.1510			0.9900	0.0183	111
45	parallel to RD*	1	0.0697	8.24	0.71	0.9621	0.0096	162
40		2	0.0635			0.9370	0.0074	146
43		4	0.0585			0.9984	0.0021	114
46		8	0.0656			0.9884	0.0068	116
41		16	0.1021			0.9650	0.0142	108
56	parallel to RD**	2	0.0455	10.08	1.57	0.9614	0.0077	146
51		4	0.0434			0.9438	0.0106	123
55		8	0.0567			0.9649	0.0042	119
58		16	0.065			0.9798	0.0073	117
Ref. [13]			0.1765	80.40		0.9622	0.0799	105

note: * Zircaloy-4 (0.6 mm thickness), ** Zircaloy-4 (2.3 mm thickness)

Hydrides parallel to the tensile stress dissolve preferentially with temperature increasing and precipitate preferentially in the direction normal to the tensile stress with temperature decreasing. The presence of hydrides has the promotive effects on hydride nucleation or growth[5]. So hydride reorientates easily with the increase of temperature cyclings under a certain stress level. If tensile stress is applied only when temperature decrease during temperature cycling, the level of hydride reorientation decreases obviously. Only when hydride dissolved at high temperature the hydride reorientation is possible[10] in its precipitattion process. The larger the difference in solubility of hydrogen during temperature cyclings is, the easier hydride reorientation is. When hydrides dissolve completely and no residual hydrides at the highest temperature during temperature cycling which do not have the promotive effects on hydride nucleation or growth[11], the level of hydride reorientation decreases too.

If grain size is smaller, the probability of habit plane distribites in the favorable direction is larger, it is easier for hydride reorientation. Too fast cooling is not favorable for hydride reorientation because of poor stress induced effect of hydirde nucleation and growth.

4 CONCLUSIONS

(1) When hydride reorientation takes place, there is a threshold stress (σ_n') which decreases with the increase of the number of temperature cycling as follows:

$$\sigma_n' = \sigma_1' - (1 - 1/n)C$$

Hydride reorientation is not obvious below the threshold stress.

(2) When applied stress is higher than threshold stress, the level of hydride re-

orientation varies with stress and the number of temperature cycling as follows:

$$R_r = R_o \exp[B \cdot n^{1/3}(\sigma - \sigma_n')]$$

where B is a constant concerned with material and experimental conditions, B is 10^{-2} MPa^{-1} in the order of magnitude under our experimental conditions.

(3) Hydride reorientation is concerned with texture, grain size, direction of applied stress, range of temperature cycling and cooling rate.

(4) Under the same condition hydride reorientation in Zircaloy-2 tube is easier than that in Zircaloy-4 tube due to the difference of texture in two kinds of tubes.

(5) Hydride reorientation in Zircaloy-4 tube takes place at the outer surface at first and then gradually to the inner surface, It might be related to the difference of the texture in outer surface and /or the different state of stress.

(6) After hydride reorientation takes place in whole section of Zircaloy-4 tube, not all hydrides change from tangential to radial distribution. So controlling texture is still effective on controlling hydride reorientation under stress.

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