

# Stress-induced reorientation of hydrides and mechanical properties of Zircaloy-4 cladding tubes

S.I. Hong <sup>a,\*</sup>, K.W. Lee <sup>b</sup>

<sup>a</sup> Department of Metallurgical Engineering, College of Engineering, Chungnam National University, Taedok Science Town, Taejon 305-764, Korea

<sup>b</sup> SEAH Besteel Co., Soryoung-dong, Kunsan City, Chunbuk 573-879, Korea

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## Abstract

Stress-induced reorientation of hydrides and its effect on the stress–strain response of Zircaloy-4 cladding tubes were investigated. The reorientation of hydrides along the radial direction was most pronounced if the tube was cooled from 300 to 200 °C under circumferential loading. Reorientation occurred much less frequently at either higher (cooled from 400 to 300 °C) or lower (cooled from 200 to 100 °C) temperature range. The population of radial hydrides in R43H7 (which was cooled from 400 to 300 °C and maintained at 300 °C for 7 h) increased drastically during annealing at 300 °C, suggesting time dependent stress-aided dissolution of circumferential hydrides and reprecipitation of radial hydrides. The drastic decrease of the strength and the complete loss of the ductility were observed in R32AC and R43H7.

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## 1. Introduction

Zircaloy-4 is known to have satisfactory mechanical strength and corrosion resistance and has been used as nuclear fuel cladding materials [1–5]. The life of zirconium alloy claddings, however, can be limited by the degradation of mechanical properties caused by cracking of brittle hydrides [6–10]. When the alloy is used in a nuclear reactor, its hydride is formed from external hydrogen sources such as waterside corrosion, dissolved hydrogen in coolant water and water radiolysis, and from internal sources such as hydrogen content in fuel

pellets and moisture absorbed by the uranium dioxide fuel pellet [11].

The extent of hydride embrittlement depends not only on the quantity of hydride present but also on its morphology and in particular the orientation of hydrides with respect to the applied stress [3,4]. For a tubular component internally pressurized in service, it is desirable to have the hydride platelets oriented with their major axis in the circumferential direction. Hydride orientation is to a large extent determined by the manufacturing process, which has a great influence on the texture and the shape and size of grains [12–14]. The cold tube reduction process (pilgering), which is used in the fabrication of cladding tubes, fortunately produces material with a strong tendency to form circumferentially oriented hydrides. However, hydrides are usually dissolved at high temperatures, and hydrogen in solid solution diffuses in the presence of concentration, temperature and

\* Corresponding author. Tel.: +82 42 821 6595; fax: +82 42 622 5850.

E-mail address: [sihong@cnu.ac.kr](mailto:sihong@cnu.ac.kr) (S.I. Hong).

stress gradients, and precipitates out as radial hydrides under the presence of the circumferential stress. In this study, the reorientation of hydrides and its effect on the mechanical properties of Zircaloy-4 tubes were studied.

## 2. Experimental procedure

Zircaloy-4 tubes used in this study were supplied by the Korea Nuclear Fuel Company. They were manufactured in the same way as the typical stress-relieved fuel claddings, and the basal poles were oriented at about  $30^\circ$  from the tube radial direction [10,15–18]. The tubes were cold-pilgered in three steps with the reduction of diameter in the final step equal to 83% and then annealed at  $460^\circ\text{C}$  for 7 h. The grain size in the transverse section was  $5.6\ \mu\text{m}$  and the length in the transverse section was  $7.9\ \mu\text{m}$ . The outer and inner diameters of the tubes were 9.4 and 8.4 mm, respectively. The chemical composition of the tube was Zr–1.34Sn–0.22Fe–0.11Cr–0.13O in weight percentage.

The tubes were charged with hydrogen using the high temperature cathodic hydrogen charging method [10]. The electrolyte solution used for hydrogen charging was 500 mg  $\text{NaHSO}_4$  (mg) + 50 mg  $\text{Na}_2\text{SO}_4$  + 10 mg  $\text{K}_2\text{SO}_4$  + 100 ml  $\text{H}_2\text{O}$ . A direct current was supplied galvanostatically to Zircaloy-4 specimens with the current density of  $0.5\ \text{A}/\text{cm}^2$ . In order to stabilize hydrogen in the specimens as hydride form, vacuum annealing was carried out at  $400^\circ\text{C}$  for 3 h after chemically cleaning of the specimen surface with acetic acid. After annealing, the tubes were cooled in air. The cooling rate for air-cooling was approximately  $126^\circ\text{C}/\text{s}$ . The amount of hydrogen pick-up after charging, assuming no loss of hydrogen, is 1260 wt.ppm [8]. The hydrogen concentration was measured using the inert gas fusion thermal conductivity detection method by LECO hydrogen analyzer RH404 (St. Joseph, Michigan, USA) and the real hydrogen concentration was 220 wt.ppm. The difference between the amount of hydrogen pick-up and the measured hydrogen concentration can be attributed to the difficulty of stabilization of hydrogen above the solubility limit and the release of over-charged hydrogen during annealing.

Ring specimens with a width of 4 mm were cut transversely from the cladding tube and the circumferential stress was applied using a special grip for reorientation treatments and tensile tests. Fig. 1 shows the schematic configuration of the ring specimen and two half-cylinders that open and strain the ring specimen. As shown in this figure, 1 mm wide space was given between two half-cylinders to allow free plastic flow during tensile testing. The diameter of the half-cylinders in Fig. 1 was 8.35 mm. Loading of the sample was applied using a United Testing Machine, SFP 10 (Huntington Beach,

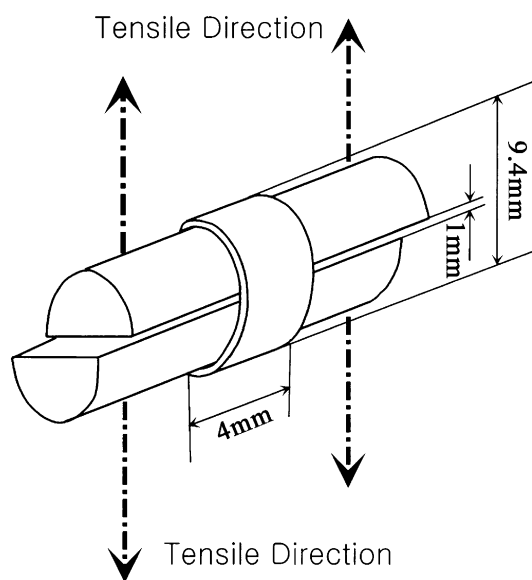


Fig. 1. Schematic configuration of tensile testing sample and grip.

CA, USA) with a three-zone split furnace. Various reorientation treatments were employed in this study. In R21AC, the specimen was heated to  $200^\circ\text{C}$  and cooled to  $100^\circ\text{C}$  at a cooling rate of  $4^\circ\text{C}/\text{min}$  under loading and air-cooled to room temperature after unloading when the temperature was lowered to  $100^\circ\text{C}$ . The loading was applied up to  $(67.5 \pm 2.5)\%$  of the yield stress at each temperature when the designated maximum temperature was reached. With cooling, the applied stress was continuously increased to keep the stress level at  $(67.5 \pm 2.5)\%$  of the yield stress throughout the cooling process in the furnace (from  $200$  to  $100^\circ\text{C}$  in case of R21AC). Likewise, in R32AC, the specimen was heated to  $300^\circ\text{C}$  and cooled to  $200^\circ\text{C}$  in the furnace at a cooling rate of  $4^\circ\text{C}/\text{min}$  under loading and air-cooled to room temperature after unloading and, in R43AC, the specimen was heated to  $400^\circ\text{C}$ , cooled to  $300^\circ\text{C}$  in the furnace under loading and air-cooled to room temperature after unloading. In R43H7, the specimen was heated to  $400^\circ\text{C}$ , cooled to  $300^\circ\text{C}$  at a cooling rate of  $4^\circ\text{C}/\text{min}$  under loading, maintained at  $300^\circ\text{C}$  for 7 h under loading and air-cooled to room temperature after unloading to examine the time dependent reorientation of hydrides.

Recently, Singh et al. [1] reported that the threshold stress for reorientation of hydrides decreased and the ratio of the threshold stress ( $\sigma_{\text{th}}$ ) to the yield stress ( $\sigma_{\text{ys}}$ ) ( $\sigma_{\text{th}}/\sigma_{\text{ys}}$ ) decreased with increasing temperature. For example,  $\sigma_{\text{th}}/\sigma_{\text{ys}}$  was reported to be approximately 0.55 and 0.4 at  $227^\circ\text{C}$  and  $327^\circ\text{C}$ , respectively [1]. The applied stress level in the present study was maintained well above the threshold stress reported for reorientation

reported by Singh et al. [1]. The gage length was determined to be 5 mm [2] after a careful comparison between the circumferential (based on the ring tensile test) and longitudinal (based on the split tube tensile test [11]) mechanical properties (yield strength and elongation). The fracture surfaces were examined using a JEOL-6400 scanning electron microscope.

### 3. Results and discussion

To ensure that the reorientation treatment was carried out at  $(67.5 \pm 2.5)\%$  level of the yield stress, the temperature dependence of the yield stress was examined. Since the yield strength increases gradually with decrease of temperature, the load was increased gradually during cooling of the sample in the furnace. Fig. 2 exhibits the hydride distribution on the radial–circumferential (RC) plane of Zircaloy-4 tube before (a) and after (b, c, d) reorientation. Fig. 3(b)–(d) show the reorientation of hydrides in R21AC (cooled from 200 to 100 °C), R32AC (cooled from 300 to 200 °C) and R43AC (cooled from 400 to 300 °C), respectively. The initial circumferential hydrides in Fig. 3(a) were formed by a high temperature cathodic charging method, followed by annealing at 400 °C for 3 h with no applied stress. Hydride precipitates have grown mostly circumferentially with some short hydrides and/or the tip of circumferential hydrides grown radially [10]. The short radial hydrides observed before reorientation treatment were suggested to result from branching of hydrides along the grain boundary

due to smaller grain dimension on the radial–circumferential (RC) plane [1].

One interesting observation is that the reorientation of hydrides was most pronounced in the R32AC sample, which was cooled from 300 to 200 °C under loading as shown in Fig. 2(c). Reorientation in R21AC and R43AC occurred much less frequently than in R32AC, but R21AC showed higher tendency for reorientation than R43AC as shown in Fig. 2(b) and (d). The hydrides formed in R43AC were much smaller than other

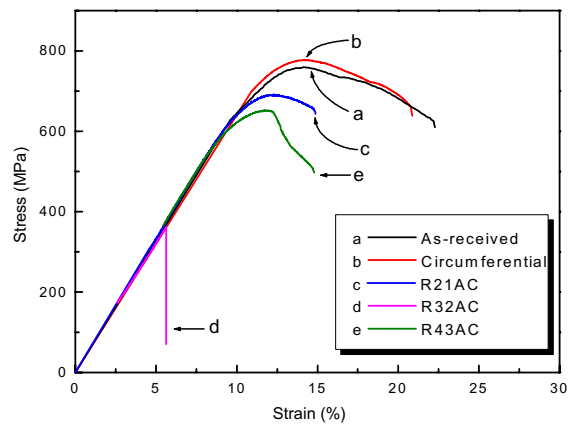


Fig. 3. Stress–strain responses of hydrided Zircaloy tubes at room temperature before and after reorientation treatment. The stress–strain responses of as-received (non-hydrided) tube are also shown for comparison.

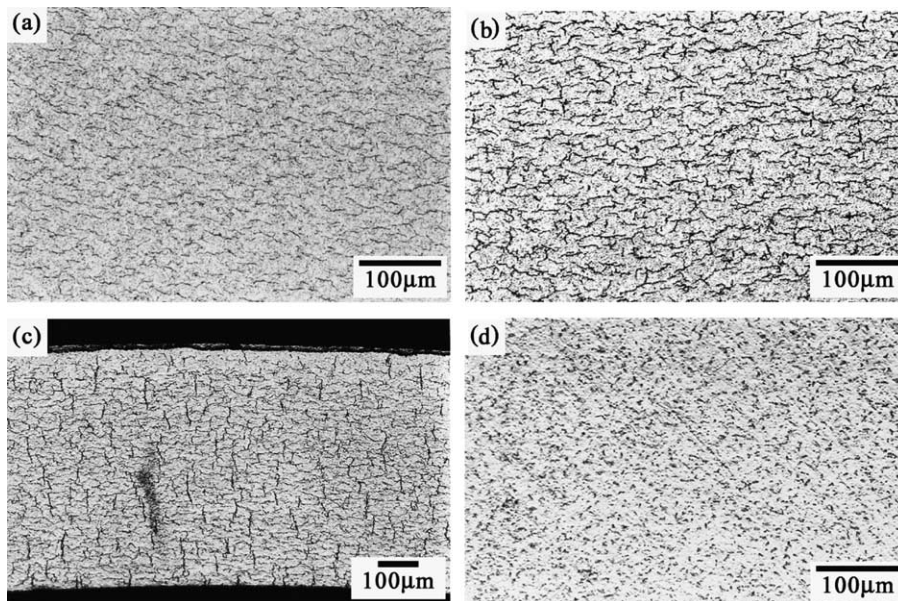


Fig. 2. Hydride distribution on the radial–circumferential (RC) plane of Zircaloy-4 tube before (a) and after (b, c, d) reorientation. (b), (c) and (d) show the reorientation of hydrides in R21AC, R32AC and R43AC, respectively.



samples, which may be associated with insufficient driving force for the precipitation and growth of hydrides in R43AC during cooling from 400 to 300 °C. The terminal solid solubility of hydrogen in Zircaloy-4 was reported to be approximately 250 and 570 ppm at 400 and 500 °C, respectively. The terminal solubility of hydrogen at 200 °C was found to be 15 ppm [1,19].

The hydrogen concentration in this study was measured to be 220 wt.ppm and hydrides are supposedly completely dissolved at 400 °C for R43AC sample. At 350 °C, the terminal solid solubility of hydrogen is approximately 150 wt.ppm, which is 70 wt.ppm lower than the hydrogen content of hydrided Zircaloy-4 of the present study. Hydrides are not likely to be reprecipitated in R43AC upon cooling since the terminal solubility of hydrogen (250 wt.ppm) at 400 °C is higher than that (220 wt.ppm) of Zircaloy-4 of the present study. Rather they are likely reprecipitated after a sufficient overcooling and some hydrides were precipitated radially under loading and most hydrides were reprecipitated circumferentially during air-cooling from 300 °C, free of loading. Circumferential hydrides precipitated during air-cooling after unloading is likely to precipitate at the former sites of coarse hydrides before thermo-mechanical treatment because of a memory effect in hydride precipitation [20–22]

At 300 °C, the terminal hydrogen solubility is approximately 75 wt.ppm [19] and supposedly 75 wt.ppm

of the hydrogen content in hydrided Zircaloy-4 would be dissolved and available for reorientation in R32AC sample cooled from 300 to 200 °C. The observation that reorientation of hydrides was much more effective in R32AC than in R43AC suggests that some circumferential hydrides which may be stable at 300 °C free of circumferential loading, may be dissolved and reprecipitated as radial hydrides during cooling from 300 to 200 °C under loading. This presumption is further supported by the time dependent reorientation of hydrides in R43H7 as will be discussed below. In R21AC, the reorientation of hydrides was limited because of the terminal solubility of hydrogen at 200 °C is 15 wt.ppm [1].

The stress–strain responses of hydrided Zircaloy tubes at room temperature before and after reorientation treatment are shown in Fig. 3. The stress–strain responses of as-received (non-hydrided) tube are also shown for comparison. The strength increased slightly whereas the ductility decreased after the formation of the circumferential hydrides. The increase of strength suggests that the circumferential hydride does not act as a fatal crack-initiating site. Rather, the Zircaloy tubes can be slightly strengthened by circumferential hydrides [5,23]. However, the ductility decreased slightly after the formation of circumferential hydrides [5]. The strength and ductility decreased with the formation of radial hydrides in R43AC and R21AC. The

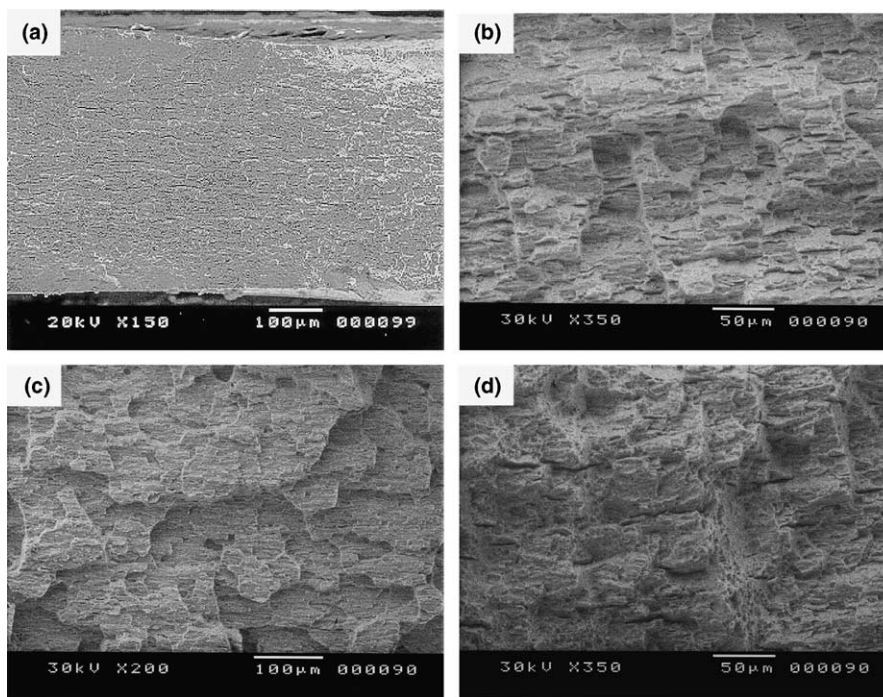


Fig. 4. Fracture surfaces of circumferentially hydrided (without reorientation treatment) (a) and reorientation-treated Zircaloy-4 tubes (b, c, d). (b), (c) and (d) show the fracture surfaces of R21AC, R32AC and R43AC, respectively.

more drastic effect of the reoriented hydrides was observed in R32AC. The strength decreased to 380 MPa and the ductility decreased to zero (it should be noted that the R32AC sample fractured in the elastic region).

Fig. 4 shows the fracture surfaces of circumferentially hydrided (without reorientation treatment, a) and reorientation-treated Zircaloy-4 tubes (b, c, d). Fig. 4(b)–(d) show the fracture surfaces of R21AC, R32AC and R43AC, respectively. The fracture surface of unhydrided Zr and its alloys is known to exhibit typical ductile fracture [2,5,23]. The circumferentially hydrided tubes exhibited ductile fracture behavior although the secondary cracks along the Zircaloy platelets are clearly visible in Fig. 4(a). The length of secondary cracks is close to the length of circumferential hydride platelet as reported by Hong et al. [2]. The fracture surfaces of R21AC (4(b)) and R43AC (4(d)) were observed to be similar to that of circumferentially hydrided sample (4(a)) with some indication of fracture along radial hydride platelet. The presence of secondary cracks (which are perpendicular to the fracture surface) suggests that there were still many circumferential hydrides in fractured R21AC and R43AC. The fracture along the radial hydride platelets (which are parallel to the fracture surface) is much more pronounced in R32AC (4(c)). Fracture surface of R32AC exhibited flat cleavage fracture along the radial hydride platelet with steps. These steps resulted from joining of brittle cracks along the radial hydride platelets on the different levels. The nil ductility of R32AC suggests that the joining of brittle radial cracks were likely to occur by the brittle fracture mostly along the circumferential hydrides.

In order to investigate the effect of loading time on the reorientation of hydrides, some specimens (R43H7) were maintained at 300 °C for 7 h after cooling from 400 to 300 °C under loading. Fig. 5 shows the hydrides on the RS (radial–circumferential) and AR (axial–radial) planes. Compared to R43AC, more pronounced reorientation of hydrides along the radial direction occurred in R43H7. This result is in contradiction with the suggestion of Northwood and Kosasih [23] that the degree of reorientation is insensitive to time under stress. As shown in Figs. 2(d) and 5, the reorientation of hydrides apparently increased with increasing loading time at 300 °C. This suggests that the dissolution of circumferential hydrides and reprecipitation of radial hydrides were favored under loading. Since the volume expands with the formation of hydrides, the hydride platelet perpendicular to the stress axis is favoured over that parallel to the stress axis. Under loading at 300 °C, the formation of radial hydrides were promoted to relieve the applied stress along the circumferential direction, which lowers the hydrogen content in the matrix and, then, promotes the dissolution of the circumferential hydrides.

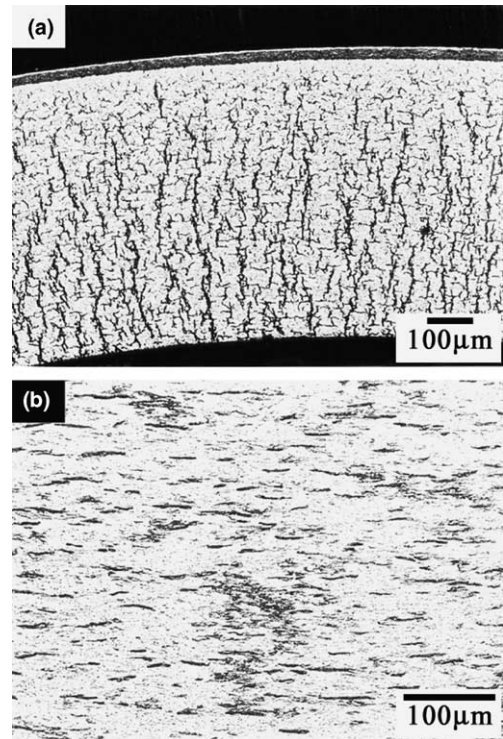


Fig. 5. Distribution of hydrides on the RS (radial–circumferential) and AR (axial–radial) planes in R43H7.

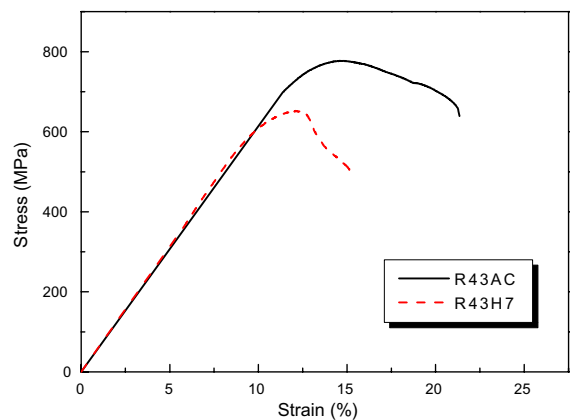


Fig. 6. Stress–strain response of R43H7 in comparison with that of R43AC. The strength and ductility of R43H7 decreased drastically, reflecting the time dependent reorientation of hydrides.

One interesting observation in Fig. 5 is the presence of a concentration gradient of hydrides toward the inside surface. The concentration gradient is likely to be linked with the local bending stress caused by the presence of 1 mm wide space given to allow free plastic flow. Upon loading, local elastic bending of the tube facing

this space may occur, which lowers the total applied stress on the outside surface by imposing the compressive stress. Higher local stress on the inside surface may have promoted denser precipitation of hydrides toward the inside surface.

In Fig. 6, the stress–strain response of R43H7 is plotted in comparison with that of R43AC. The strength and ductility of R43H7 decreased drastically, reflecting the time dependent reorientation of hydrides. The strength decreased to  $\approx 350$  MPa and the ductility decreased to zero. It should be noted that the population of radial hydrides in R43H7 is extremely high. The radial hydrides and the Zr matrix would experience the iso-stress loading condition under the circumferential loading, resulting in the premature cracking along the radial hydrides due to negligible ductility of hydrides at room temperature.

#### 4. Conclusions

In this study, stress induced reorientation of hydrides in Zircaloy-4 cladding tubes were investigated and the following conclusions were obtained.

1. The reorientation of hydrides was most pronounced in the R32AC sample, which was cooled from 300 to 200 °C under loading. Reorientation occurred much less frequently in R21AC (cooled from 200 to 100 °C under loading) and R43AC (cooled from 400 to 300 °C under loading).
2. The fracture surface of R32AC exhibited a flat cleavage fracture along the radial hydride platelet with steps. The fracture surfaces of R21AC and R43AC exhibited dimples and secondary cracks with some brittle fracture along radial hydride platelets.
3. The reorientation of hydrides was found to increase with heat treating at 300 °C for 7 h under loading, which strongly supports the time-dependent reorientation of hydrides in Zircaloy-4. In this sample, the strength decreased to  $\approx 380$  MPa and the ductility decreased to zero.

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