

## Driving Force for Precipitation of Hydrides and Their Precipitation Behavior in Zirconium Alloys

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### 1. Introduction

The size and shape of hydrides are well known to change with cooling rate after homogenization treatments to dissolve hydrides. For example, when Zr-2.5Nb with 60 ppm hydrogen is water quenched (WQ-) or furnace-cooled (FC-) after homogenization at 302°C for 30h, the shape and size of hydrides are well-known to be different: small and needle-shaped hydrides are observed in the WQ-Zr-2.5Nb specimen while large and plate-shaped hydrides appear in the FC-Zr-2.5Nb specimen [1]. Furthermore, depending on homogenization temperature, the size and distribution of hydrides changed despite the identical cooling conditions being applied [2]. However, the reasons remain unknown. The old DHC model [3] claims that hydrogen accumulates at a crack tip under the stress gradient enough to exceed the solubility of hydrides for precipitation (or TSSP) and then hydrides precipitate there, leading to cracking. Considering that DHC cannot occur at test temperatures above 180°C when it is approached directly by heating, their claims are questionable. Considering that the molar volume of hydrides precipitated in the zirconium matrix is higher by 17.5% than that of the matrix, hydrides cannot be precipitated in the zirconium matrix unless there is a room available for the hydrides with a higher molar volume. However, the old DHC model [3] cannot explain how to accommodate the volume misfit created by hydrides. Moreover, it cannot explain why the size and shape of hydrides change with cooling rate after homogenization, and homogenization temperature, as described above.

The aim of this work is to show that the size and distribution of hydrides are determined by the degree of ordering occurring in the zirconium matrix the rate of which depends on not only cooling rate after homogenization but also homogenization temperature under the identical cooling condition. To this end, we examined how hydrides precipitate during cooling using differential scanning calorimetry (DSC) and SEM.

### 2. Results and discussion

#### 2.1. Physical significance of dissolution and precipitation of hydrides

Figs. 1 and 2 show typical results obtained by DSC and dynamic elastic modulus techniques (EDM) both of which were used to determine the temperatures of the

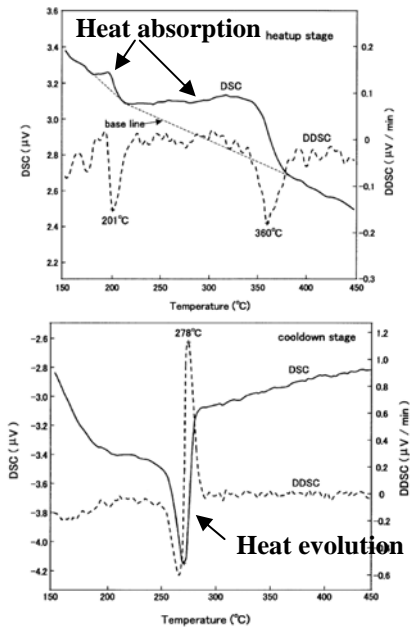


Fig. 1. Typical DSC and time derivative curves for a Zircaloy-2 specimen containing 106 ppm hydrogen obtained during heat-up and cool-down [4].

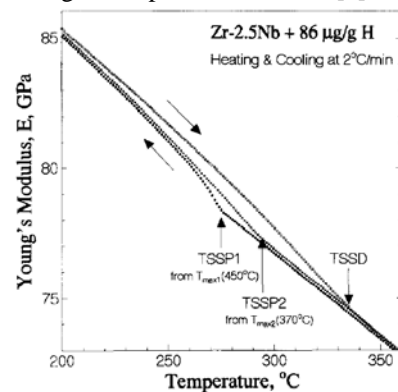


Fig. 2. Typical curves of Young's modulus  $E$  versus temperature for a Zr-2.5Nb specimen containing 86 ppm (0.77 at.%) of hydrogen [5].

terminal solid solubility of hydrogen for precipitation and dissolution (TSSP and TSSD) [4,5]. As shown in Fig.1, upon heating, two endothermic peaks were observed at around 200°C and in a wide temperature range from 215 to 380°C from Zircaloy-2 with hydrides that had been furnace-cooled after hydrogen charging [3]. Considering that heat absorption is related to the disordering phase transformation to transform order to disorder like the solid to liquid transformation, hydride dissolution upon heating represents disordering. By

contrast, upon cooling, an exothermic peak was observed. As heat evolution is related to the ordering transformation from disorder to order, hydride precipitation represents the ordering. In other words, hydride precipitation occurs by ordering. This means that hydride cannot precipitate without ordering. Specifically, hydrides cannot precipitate by simply increasing the local hydrogen concentration at the crack tip to the TSSP without ordering, as claimed by the old DHC model [3]. As shown in Fig.1, considering that heat evolution occurring only upon cooling means ordering, the hydride phase formed upon cooling is the ordered phase. Conversely, hydride dissolution corresponds to the disordering of zirconium alloys. Compelling evidence that hydrides are the ordered phase is an increase in Young's modulus of the zirconium matrix upon precipitating of hydrides, as shown in Fig. 2 [4]. Conversely, the hydride dissolution is the disordering of the zirconium matrix, leading to a decrease in its Young's modulus. In short, ordering increases the Young's modulus of the zirconium matrix, leading to precipitation of hydrides while disordering decreases Young's modulus, leading to dissolution of hydrides. An increase or decrease in Young's modulus corresponds to the increase or decrease in the hardness of the zirconium matrix by ordering or disordering.

## 2.2. Effect of homogenization temperature

Fig. 3 shows the morphology of hydrides in a Zr-2.5Nb containing 81 to 86 ppm H with homogenization temperature followed by furnace-cooling: (a) 350°C for 500h, (b) 400°C for 240h and 475°C for 240h [2]. The long and plate-shaped hydrides were observed when the homogenization temperature decreased to 350°C. However, with increasing homogenization temperature, the precipitated hydrides were short and more randomly distributed. The different shape and distribution of hydrides precipitated in the Zr-2.5Nb with homogenization temperature, as shown in Fig. 3, is related to the degree of ordering during cooling from the homogenization temperature. The results of Fig. 3 show that the degree of ordering during cooling was higher with decreasing homogenization temperature. In other words, during slow cooling from 350°C, the rate of ordering was high enough to generate high compressive stresses in the zirconium matrix, causing plate-shaped hydrides to nucleate and grow. With homogenization temperature increasing from 350°C to 400 or 475°C, disordering proceeded fast enough to generate the higher degree of disorder during homogenization. During slow cooling, the ordering rate was retarded,

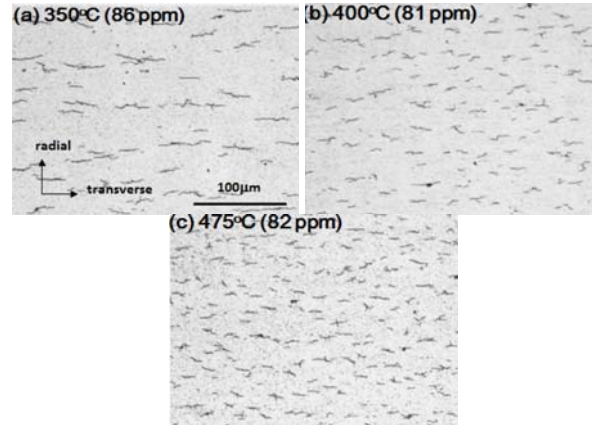


Fig. 3. Hydride morphology in Zr-2.5Nb containing 81 to 86 ppm hydrogen furnace-cooled after homogenization at (a) 350°C, (b) 400°C and 475°C [2].

generating low compressive stresses in the zirconium matrix. As a result, short and needle-shaped hydrides were precipitated, as shown in Fig. 3b and 3c. Compelling evidence for this rationale is provided by our observations that small and needle-shaped hydrides are observed in WQ-Zr-2.5Nb with disorder while large and plate-shaped hydrides appear in a FC-Zr-2.5Nb with order [1].

## 4. Conclusions

Hydrides precipitate in zirconium by ordering, which is a new discovery. This is evidenced by a change in Young's modulus and the accompanied heat evolution. The morphology of hydrides is controlled by the ordering rate that determines the level of compressive stresses generated in the zirconium matrix. The lower compressive stress promotes nucleation of needle-shaped hydrides while the higher compressive stress causes the nucleated hydrides to grow into plate-shape. Given these new findings, the claims of the old DHC model turns out to be evidently invalid.

## REFERENCES

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