

## On the Origin of Precipitation of Hydrides in Zirconium Alloys

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### 1. Introduction

It is well-known that the size and shape of hydrides 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, 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]. However, the reasons remain unknown. Given that the morphology transformation of carbides from needles to plates also takes place in carbon steels [2], the morphology and phase transformations of hydrides are a general phenomenon that can occur in materials.

The old DHC models [3,4] claim 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. Despite the fact that the molar volume of hydrides precipitated in the zirconium matrix is higher by 17.5% than that of the matrix, the old DHC models [3,4] 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 [1], and homogenization temperature [5]. The aim of this work is to show that precipitation of hydrides is related to an entropy decrease, which generates autogenously compressive stresses in materials.

### 2. Results and discussion

#### 2.1. Physical significance of heat evolution and absorption

To determine the temperatures of the terminal solid solubility of hydrogen for precipitation and dissolution (TSSP and TSSD) [6,7], differential scanning calorimetry (DSC) methods and dynamic elastic modulus techniques (EDM) have been employed. Figs. 1 and 2 show the experimental results obtained from zirconium alloys containing hydrogen. 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 for Zircaloy-2 with 106 ppm H with hydrides that was furnace-cooled after hydrogen charging [6]. In contrast, on cooling, heat was evolved

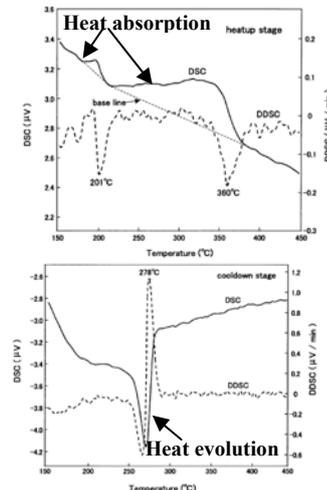


Fig. 1. Typical DSC and time derivative curves for a Zircaloy-2 specimen containing 106 ppm hydrogen obtained during heat-up and cool-down [4].

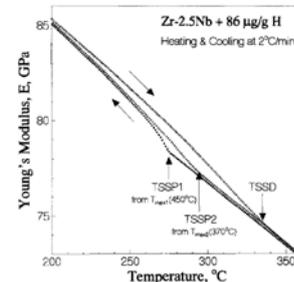


Fig. 2. Typical curves of Young's modulus E versus temperature for a Zr-2.5Nb specimen containing 86 ppm (0.77 at.%) of hydrogen [5].

from the Zircaloy-2 containing 106 ppm H. According to the second thermodynamics law, entropy is defined as the amount of heat released or absorbed divided by temperature ( $\Delta S=Q/T$ ). Thus, heat evolution means an entropy decrease whereas heat absorption a entropy increase. Given that the entropy decrease generates a volume decrease, it produces compressive stresses. In other words, heat evolution leads to an entropy decrease, spontaneously generating compressive stresses in materials. The compressive stresses generated by the entropy decrease are the driving force to compress the zirconium matrix and make a room for hydrides with a higher molar volume to precipitate in the matrix of zirconium with a lower molar volume. This explains why the precipitation of hydrides always accompanies heat evolution, representing the entropy decrease. Since the entropy decrease means ordering, heat evolution provides compelling evidence for the

occurrence of ordering. In other words, the precipitation of hydrides is driven by the compressive stresses arising from the entropy decrease or 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 given by 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, 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

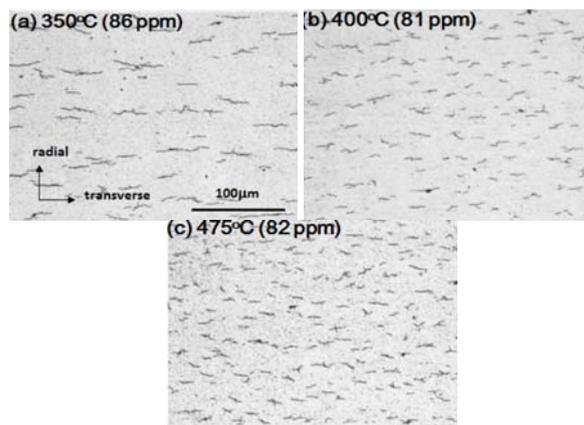


Fig. 3. Hydride morphology in Zr-2.5Nb containing 81 to 86 ppm hydrogen furnace-cooled after homogenization at (a) 350°C, (b) 400°C and 475°C [2].

are precipitated 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 magnitude of compressive stresses arising from entropy decrease 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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