Physical Understanding of Precipitation and Dissolution of Hydrides in Zirconium Alloys

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1. Introduction

Hydrides are precipitated in zirconium alloys during their operating in reactors, leading to their embrittlement and delayed hydride cracking (DHC). Thus, an understanding of the precipitation process of hydrides and their properties is very important in maintaining the mechanical integrity of zirconium alloys during their operation in reactors and dry storage of spent nuclear fuels. However, the precipitation process of hydrides is controversial. The old DHC models [1,2] 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. In fact, the physical understanding of precipitation and dissolution of hydrides remains lacking although they are determined using various techniques: differential scanning calorimetry (DSC), internal friction and dynamic elastic modulus. The aim of this study is to understand the physical meaning of precipitation and dissolution of hydrides and what controls the morphology of hydrides precipitated in zirconium alloys.

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 terminal solid solubility of hydrogen for precipitation and dissolution (TSSP and TSSD). As shown in Fig.1, upon heating up, 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 from order to disorder like the solid to liquid transformation, hydride dissolution upon heating represents the 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.
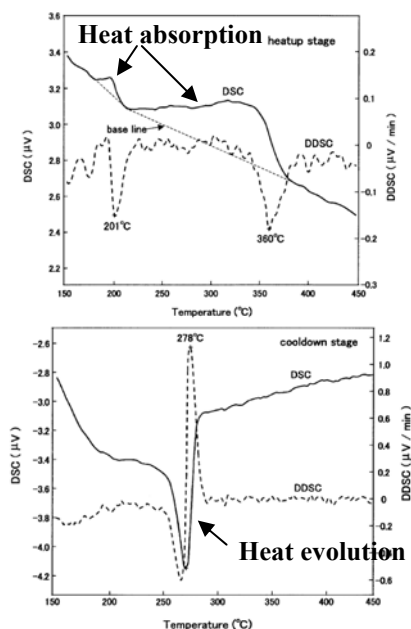

Fig. 1. Typical DSC and time derivative curves for a Zircaloy-2 specimen containing 106 ppm hydrogen obtained during heat-up and cool-down [3].
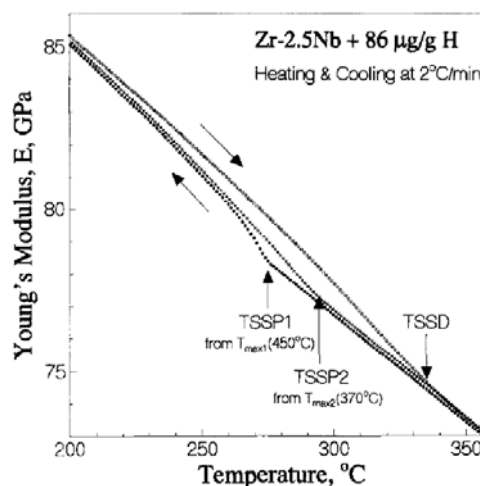

Fig. 2. Typical curves of Young's modulus E versus temperature for a Zr-2.5Nb specimen containing 86 ppm (0.77 at.%) of hydrogen [4].

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 models. 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 Young's modulus, In short, ordering increases Young's modulus, 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. Phase and shape of hydride with cooling rate

Fig. 3 shows the morphology of hydrides in Zr-2.5Nb containing 60 ppm H after water-quenching and furnace cooling, respectively, following annealing at $302^{\circ}C$ for 30 h. Furnace-cooling and water quenching generated plate- and needle-shape hydrides, respectively, which agrees perfectly the published results [5]. Nevertheless, it remains why the morphology of hydrides were different with cooling rate. Considering that ordering occurs during furnace cooling in the zirconium matrix, however, the zirconium matrix becomes harder upon furnace-cooling, as revealed by an increase in Young's modulus (Fig. 2). When hydride with a larger molar volume precipitates in the harder zirconium matrix, the hydride must be soft enough to accommodate the strain energy resulting from a change in the molar volume, transforming to plate shape upon precipitation, as shown in Fig. 3. In fact, Lee [6] has also shown that an elastically soft precipitate tends to have an equilibrium morphology of low symmetry such as a plate. By contrast, during water quenching, no ordering occurred in the zirconium matrix, which is rather soft. During precipitation, hard hydrides can be precipitated in the soft zirconium matrix, transforming to needle shape, as shown in Fig. 3. In short, a change in the morphology of hydrides with cooling rate, as shown in Fig. 3, is related to the atomic arrangement of the zirconium matrix which can take place during cooling: the hard zirconium matrix due to ordering during furnace cooling causes precipitation of plate-shape hydrides while the soft one due to disordering during water quenching does precipitation of needle-shape hydrides, as shown in Fig. 3. .

4. Conclusions

Precipitation and dissolution of hydrides occur by ordering and disordering, respectively, of the zirconium matrix containing hydrogen. Given these new findings, the claims of the old DHC models that hydrides precipitate by increasing the local concentration of hydrogen to the TSSP in isothermal conditions are clearly invalid. Precipitation of hydrides occurs only by ordering, which is evidenced by a change in Young's modulus. The morphology of hydrides is controlled by the hardness of the zirconium matrix which is determined by the occurrence of ordering during cooling.
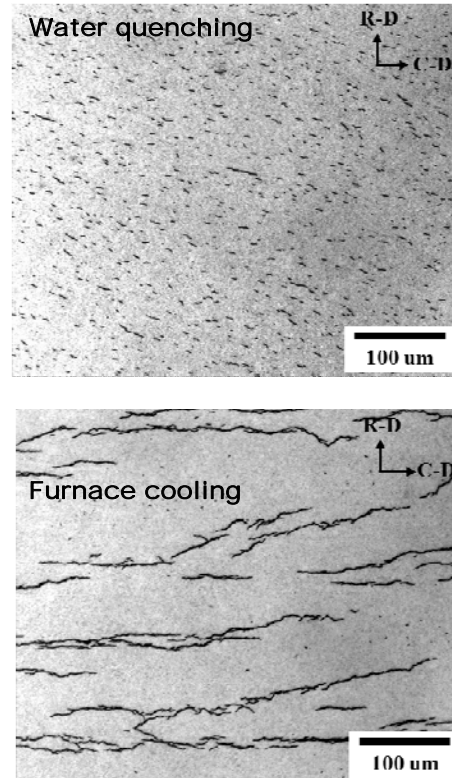

Fig. 3. Morphology of hydrides precipitated in Zr-2.5Nb with cooling rate after solution annealing at $302^{\circ}C$.

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