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Can Naonocrystalline Zirconium Suppress Hydride Precipitation?

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1. Introduction

Hydride embrittlement is a significant concern in nuclear fuel cladding, as it can lead to mechanical failure. Hydrogen, generated through the corrosion of cladding material in contact with the coolant, diffuses into the cladding and precipitates as hydrides once its concentration surpasses the terminal solubility (TSS) limit. These hydrides, which preferentially nucleate along grain boundaries (GBs), severely degrade the material's mechanical properties. The embrittlement effect is particularly pronounced under low-temperature conditions, where the TSS is lower, making hydride behavior a critical factor in evaluating the safety of spent nuclear fuel storage. [1]

Previous studies have indicated a correlation between grain size and hydride precipitation behavior. Sangbum Kim et al. [2] demonstrated that in zirconium-based alloy cladding tubes, the welding zone exhibits suppressed hydride precipitation. Their findings further revealed that among all regions of the cladding tube, the weld zone possesses the smallest grain size, suggesting a potential relationship between grain refinement and hydride suppression.

This study aims to mitigate hydride precipitation by employing a nanocrystalline structure with grain sizes ranging with submicron and nanoscale grain sizes. The microstructural characterization and assessment of hydride precipitation are conducted using optical microscopy (OM), scanning electron microscopy (SEM), and electron backscatter diffraction (EBSD).

2. Theoretical Background

2.1. Hall-Petch Relation

Nanocrystalline metals exhibit an increase in GB density as grain size decreases, which impedes dislocation movement, as demonstrated by Shu et al. [3]. This leads to an accumulation of dislocations at GBs, resulting in an overall increase in yield stress, as described by the Hall-Petch relation:

$$(1)\quad \sigma_y = \sigma_0 + \frac{k}{\sqrt{d}}$$

where σ_y represents the yield stress, σ_0 denotes the intrinsic stress required for dislocation movement, k is a material-dependent constant, and d is the grain size. Hoon Lee et al. [4] have reported that an increase in hydrogen concentration progressively reduces the yield stress of both Zirlo and Zircaloy-4 alloys.

2.2. Thermodynamic Modeling

The thermodynamic model of hydride precipitation elucidates the influence of grain size on hydride formation. As depicted in Fig. 1, the process begins with hydrogen dissolution in the Zr matrix and culminates in hydride precipitation along GBs. The change in Gibbs free energy associated with this transformation is expressed as follows [5]:

$$(2)\quad \Delta G = V\{-\Delta G_{\text{chem}} + \Delta G_{\text{strain}}\} + A\Delta G_{\text{interface}} - S\Delta G_{\text{GB}}$$

where ΔG_{chem} represents the chemical free energy change per unit volume, ΔG_{strain} corresponds to the strain energy per unit volume associated with hydride formation at GBs, $\Delta G_{\text{interface}}$ accounts for the interfacial energy between the α-Zr matrix and hydride nucleus, and ΔG_{GB} denotes the reduction in free energy due to intergranular hydride precipitation. The variables V, A, and S represent the nucleus volume, interfacial area, and GB area, respectively [5].

To develop a simplified model, only the elastic regime—where the material returns to its original shape upon stress removal—is considered. Assuming that hydride precipitates in similar quantities and sizes in both nanocrystalline and conventional microstructures, the total hydride volume and Zr-hydride interface remain constant. Consequently, ΔG_{strain} becomes the dominant variable influencing ΔG. By integrating the Hall-Petch relation into the strain energy model proposed by Lee et al. [6], ΔG_{strain} is found to be inversely proportional to the square root of the grain size. This implies that reducing grain size increases ΔG, thereby inhibiting hydride precipitation.

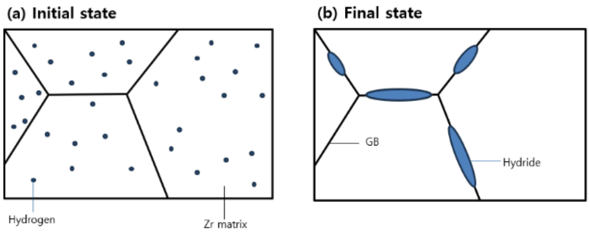

Fig. 1. Schematic of the microstructure for (a) the unprecipitated state and (b) hydride precipitated state in Zr alloys

3. Experimental Setup

3.1. Alloying

Nanocrystalline materials with extremely fine grains are prone to grain growth due to their high surface area-to-volume ratio, which accelerates atomic diffusion. To stabilize grain size, alloying was employed, following the approach suggested by Chookajorn et al. [7]. Building upon the thermodynamic principles of nanocrystalline alloy design, Wagih et al. [8] identified stable alloying elements for Zr. Based on their findings, this study incorporates 7 wt.% Cu into Zr to enhance microstructural stability.

3.2. Nanocrystal Formation

A Zr-Cu alloy is synthesized by blending Zr and Cu powders in an argon atmosphere at a 93:7 weight ratio. The mixed powders undergo high-energy ball milling, which induces severe plastic deformation and refines grain structure through repeated collisions. The resulting powder is subsequently consolidated via hot isostatic pressing (HIP) under high-temperature, high-pressure conditions, producing a dense nanocrystalline material suitable for further analysis.

3.3. Hydride Precipitation

Hydrogen charging experiments are conducted to examine hydride precipitation in the prepared specimens. A mass flow controller regulates the temperature and hydrogen pressure within the reaction chamber. High-pressure hydrogen (400 torr) is injected into the system and maintained at equilibrium. The difference between the initial and final hydrogen pressure is used to estimate the hydrogen concentration within the specimens. Finally, OM, SEM, and EBSD techniques are utilized to characterize the microstructure and assess the extent of hydride precipitation.

4. Conclusion

This study explores the potential of nanocrystalline Zr-Cu alloys to suppress hydride precipitation by reducing grain size to the 10–100 nm range. Theoretical analyses based on Gibbs free energy calculations and the Hall-Petch relation indicate that smaller grains thermodynamically hinder hydride formation. To validate this hypothesis, a nanocrystalline Zr-Cu alloy is fabricated, and its hydride precipitation behavior is systematically examined. The findings of this research contribute to the advancement of nuclear fuel cladding materials with improved resistance to hydride embrittlement, thereby enhancing the safety and longevity of spent nuclear fuel storage systems.

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