

Investigation of High Temperature Hydrogen Degradation of Structural Materials in Nuclear Energy System

Jun Yeong Jo^a, Hwasung Yeom^{a*}

^aDivision of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 37673, Republic of Korea

*Corresponding author: hyeom@postech.ac.kr

***Keywords : Hydrogen Embrittlement, High Temperature Hydrogen Attack, Hydrogen Permeation**

1. Introduction

Hydrogen is considered one of the most promising clean energy sources, offering a sustainable solution to global climate change. As the portion of hydrogen energy continues to grow worldwide, many countries are expanding their hydrogen infrastructure to ensure a stable supply system. In particular, the nuclear industry is gaining attention for its potential to produce hydrogen using high-temperature steam from the reactors. For example, High-Temperature Gas-Cooled Reactors (HTGR) are classified as Generation IV reactors, offer significant potential for hydrogen production [1]. These methods are considered as promising approaches to achieving carbon neutrality while also enhancing energy security. In this context, extensive research has been conducted, and numerous studies are currently underway to develop efficient hydrogen production, storage, and transport technologies.

A key challenge in advancing hydrogen technology is ensuring the reliability and durability of structural materials used in hydrogen systems. Structural materials commonly used in high temperature hydrogen environments include SS304, SS316, Crofer 22 APU. SS304 and SS316 are austenitic stainless steels with an FCC structure, offering strong resistance to hydrogen embrittlement, excellent weldability, and corrosion resistance. Crofer 22 APU is known for its high-temperature stability up to 900 °C and has excellent corrosion resistance due to the formation of a chromium-manganese protective oxide layer. Additionally, it has high electrical conductivity and a low thermal expansion coefficient, making it a suitable structural material for solid oxide electrolysis (High temperature water electrolysis) cell interconnects (which uses high temperature steam generated from nuclear power plants).

However, despite the advantages, the structural materials used in hydrogen environments are still susceptible to hydrogen-induced degradation, including embrittlement and permeability issues, particularly under high-temperature and high-pressure conditions. Notably, in most high-temperature hydrogen process systems, structural materials are often exposed to hydrogen concentration gradients [2]. One side may be in a low-hydrogen environment (e.g., air), while the other is exposed to a high-hydrogen or wet hydrogen ($H_2 + H_2O$) atmosphere. Compared to single-gas environments (O_2 ,

H_2 , etc.), dual atmospheres can cause unexpected corrosion behaviors and accelerate degradation rates. According to previous studies, in dual-atmosphere environments where a hydrogen concentration gradient is present, hydrogen diffusion through the base metal can lead to hydrogen penetration into the chromium oxide layer on the opposite side, where it reacts with oxygen. Consequently, an increase in Cr vacancies promoted Fe ion dissolution, potentially weakening the structural and chemical stability of the protective oxide layer [3]. Therefore, further research on revealing the mechanisms of material degradation and developing mitigation strategies, such as effective hydrogen-resistant coatings or alternative alloys, is essential to ensure long-term stability and safety in hydrogen-related applications.

To manage hydrogen diffusion through metallic materials, several research are being conducted on the application of thin hydrogen permeation barrier coatings on structural materials. These coatings aim to reduce hydrogen adsorption and provide high hydrogen permeation resistance. They must be free from structural defects such as pores and cracks. Previous studies have demonstrated that applying ceramic hydrogen permeation barrier coatings (e.g., Al_2O_3 , Er_2O_3 , TiN, SiC, ZrO_2 , Cr_2O_3 , Y_2O_3) to the material surface can effectively delay or prevent hydrogen diffusion [4]. However, research on using metallic hydrogen permeation barriers with mechanical properties similar to the metal substrate remains has not been widely conducted

In this paper, we present the research plan for hydrogen degradation experiments designed to investigate the fundamental mechanisms of hydrogen degradation in materials, including hydrogen permeation and to develop mitigation technologies.

2. Experimental

2.1 Simulated Condition for High-Temperature Hydrogen Degradation

The selected materials in this study include SS304, SS316, Crofer 22 APU. To put the samples in the hydrogen gas environment, the furnace and sample holder are designed like Fig 1. The hot furnace is placed around the quartz tube to heat up the gas environment. The samples are fabricated into coin shape disk, and

positioned in the sample holder, which are designed to separate the type of contacting gas from inside and outside of the specimen. By separating the gas environment, the hydrogen gradient through the specimen can be formed. For the dual-atmosphere experiment, the gas environment will consist of ambient air outside the sample holder, while the inside will be composed of $\text{Ar}+\text{H}_2$ or $\text{Ar}+\text{H}_2+\text{H}_2\text{O}$. In the single-atmosphere experiment, both the inside and outside of the sample holder will be filled with the same $\text{Ar}+\text{H}_2$ mixture. Consequently, in the dual-atmosphere experiment, hydrogen will diffuse through the sample toward the air-exposed side, influencing the oxidation behavior of the material. The test will be conducted at temperatures ranging from 400 °C to 800 °C in 100 °C intervals.

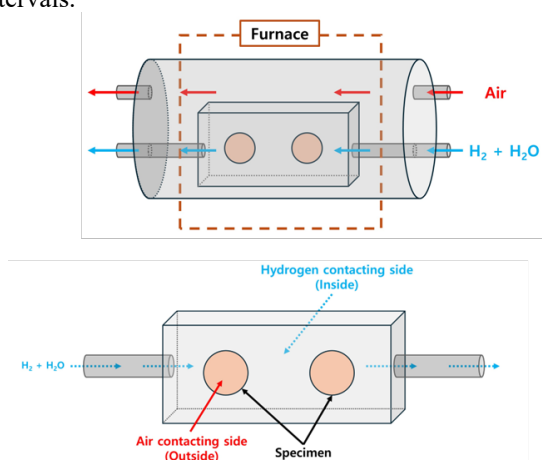


Fig. 1. Scheme of hydrogen degradation experimental facility

2.2 Measurement of hydrogen permeability

To evaluate the permeability of each material, a time-lag test will be conducted. Hydrogen will permeate through the specimen due to the pressure difference between the inlet and outlet. By measuring the increase in outlet pressure, the permeability of the material can be indirectly determined. The test will be performed at temperatures ranging from 400 °C to 800 °C in 100 °C intervals to investigate the effect of temperature on material permeability.

Following the test, post-experimental analysis will focus on microstructural changes (grain size, dislocation density, hydrogen bubble formation), oxidation characteristics (oxide layer thickness, spallation, cracking), and mechanical properties (hardness, yield strength, ductility) to provide a comprehensive understanding of degradation mechanisms.

3. Future work

Until now, organizing an experimental facility for simulating high temperature hydrogen degradation is on progress. In our future study, to mitigate hydrogen permeation and improve oxidation resistance, a Cr

coating which has excellent hydrogen barrier properties will be deposited onto the substrate using a cold spray coating technique. This study will aim to evaluate the effectiveness of this coating in reducing hydrogen permeability and to investigate the underlying mechanisms. The findings from this research are expected to contribute to improving the reliability, durability and performance of structural materials used in high-temperature hydrogen processes, such as high-temperature electrolysis and hydrogen-based iron reduction, or in nuclear energy system.

REFERENCES

- [1] Boretta, A. (2023). Hydrogen production by using high-temperature gas-cooled reactors. *International Journal of Hydrogen Energy*, 48(21), 7938-7943.
- [2] Wu, Y., He, D., Li, S., Liu, X., Wang, S., & Jiang, L. (2016). Deuterium permeation properties of $\text{Y}_2\text{O}_3/\text{Cr}_2\text{O}_3$ composite coating prepared by MOCVD on 316L stainless steel. *International Journal of Hydrogen Energy*, 41(18), 7425-7430.
- [3] Rufner, J., Gannon, P., White, P., Deibert, M., Teintze, S., Smith, R., & Chen, H. (2008). Oxidation behavior of stainless steel 430 and 441 at 800 °C in single (air/air) and dual atmosphere (air/hydrogen) exposures. *International Journal of Hydrogen Energy*, 33(4), 1392-1398.
- [4] Zhang, G., Wang, X., Xiong, Y., Shi, Y., Song, J., & Luo, D. (2013). Mechanism for adsorption, dissociation and diffusion of hydrogen in hydrogen permeation barrier of $\alpha\text{-Al}_2\text{O}_3$: A density functional theory study. *International journal of hydrogen energy*, 38(2), 1157-1165.