

MH 수소저장 장치의 방출시 열거동 모사 수치 모델 개발

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Development of a Thermal Model for Discharge Behavior of MH Hydrogen Storage Vessels

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ABSTRACT

Metal hydride alloys are a promising type of material in hydrogen storage applications, allowing for low-pressure, high-density storage. However, while many studies are being performed on enhancing the hydrogen storage properties of such alloys, there has been little research on large-scale storage vessels which make use of the alloys. In particular, large-scale, high-density storage devices must make allowances for the inevitable generation or absorption of heat during use, which may negatively impact functioning properties of the alloys. In this study, we develop a numerical model of the discharge properties of a high-density MH hydrogen storage device. Discharge behavior for a pilot system is observed in terms of temperature and hydrogen flow rates. These results are then used to build a numerical model and verify its calculated predictions. The proposed model may be applied to scaled-up applications of the device, as well as for analyses to enhance future device designs.

KEY WORDS : Numerical analysis(전산 모사), Metal hydrides(수소화 합금), Hydrogen storage(수소 저장), Thermal model(열 해석 모델)

1. Introduction

Hydrogen storage is a major issue which must be resolved for development of a viable, efficient

hydrogen economy¹⁾. Many storage technologies including high pressure gas or liquid-state storage are hindered by issues such as low volumetric storage density, systemic instability and cost. Certain metal alloys have been shown to be a promising alternative, with many numerous

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previous studies demonstrating their ability to absorb and release hydrogen in significant quantities. Moreover, hydrogen storage in metal hydrides offers potential benefits such as high volumetric density and stable, low pressure utilization¹⁾. One type of alloy with promising hydrogen storage properties is the TiCrV alloy^{2,3)} and TiCrV-Fe alloy⁴⁾. These alloys have been shown to demonstrate high reversible storage capacities and resiliency through multiple cycles.

However, utilization of these alloys in practical applications has been hindered by the comparatively low volume of research being performed on their bulk behavior or storage device designs for such materials in large-scale applications. Moreover, high costs and low practicality make it difficult to perform experimentation on large-scale devices or systems. This is particularly true in a climate with domestic investment in hydrogen research being more heavily focused on production than on storage or distribution⁵⁾.

In this study, we address this issue by developing a numerical analysis model of the discharge properties of an MH storage system based on measured properties from a pilot system using TiCrV-Fe alloy. The numerical modeling takes into account key parameters such as the inevitable absorption of heat during hydrogen release, which may negatively impact the storage properties of the alloy^{1,6,7)}.

The model allows for prediction of the thermal behavior of an MH vessel during hydrogen release, and may be applied to different configurations of MH systems, and in further studies to enhance future device designs.

2. Experimental Method

2.1 Pilot System

In order to obtain bulk-scale data of the TiCrV-

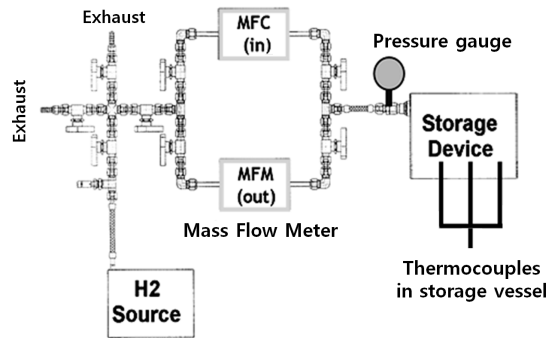


Fig. 1 Pilot system for bulk-scale data acquisition.

Fe alloy used in the present study, we built a pilot system with a simple hydrogen storage device based on prior simulations intended to optimize both reaction rates and temperature control. The system, as illustrated in Figure 1, makes it possible to obtain temperature readings from various locations within the hydride beds by employing strategically placed thermocouples, as well as gas flow rates for both absorption and desorption through a mass flow controller .

2.2 Numerical Modeling

Because of limitations arising from high cost and practicality, production of large amounts of alloys and direct experimentation on multiple devices utilizing them is prohibitively difficult. As a result, studies regarding the impact of certain variables on device efficiency are often limited to a single design⁷⁾.

A convenient and effective alternative to direct experimentation is to predict the behavior of systems in question using numerical simulation. Several studies adopting this method have been reported in the literature⁸⁻¹¹⁾. Unfortunately, most of these studies are not performed in tandem with direct analysis of real alloy samples. In this study, bulk material properties are first obtained from a

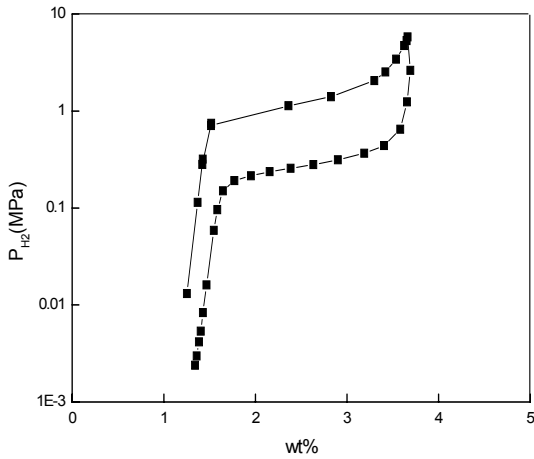


Fig. 2 PCT curve for $\text{Ti}_{0.32}\text{Cr}_{0.35}\text{V}_{0.25}\text{-Fe}_{0.08}$ alloy at 293K.

pilot system to create an accurate and reliable numerical model.

The simulations are based on measurements taken from $\text{Ti}_{0.32}\text{Cr}_{0.35}\text{V}_{0.25}\text{-Fe}_{0.08}$ alloy. The PCT characteristics of the alloy at 293K are given in Figure 2. The alloy demonstrates a relatively high reversible storage capacity within a reasonable pressure range.

The reaction heat value used in this study was measured in alloy samples to be 42 kJ for each mol of hydrogen gas. Temperature for the system is calculated by multiplying this value by the flow rate, which is assumed to be equal to the reacted amount of hydrogen.

The effective thermal conductivity of the device is of particular importance in determining the efficiency of a device^{1,6,7,12}, especially given the unpredictable conductivity of porous materials^{12,13}. We have determined the conductivity of a porous bed of the MH alloy to be approximately 0.2 W/m-K.

A number of assumptions are made in order to simplify the model and improve calculation efficiency:

(i) As pointed out in earlier studies¹⁴, metal

hydride materials will generally reach a uniform particle size following several cycles of hydrogenation and dehydrogenation, and therefore the powder bed is assumed to be a homogeneous volume of uniform porosity.

(ii) Because of the extremely high diffusivity of hydrogen gas and the high porosity of metal hydride beds, the entire metal hydride bed region is assumed to undergo reaction simultaneously. This simplification is applicable in this study as we deal mostly with relatively small mobile application-scale devices, but may not be suitable for scaled-up applications.

(iv) In order to simplify the model, reaction kinetics are not directly calculated. Instead, we base our modeling and design on considerations of heat, given the measured reaction heat of 42 kJ for each mol of hydrogen gas.

Heat transfer is calculated through an energy conservation equation. Such an equation may be defined in numerous ways, but the calculations performed in the present study make use of the total enthalpy equation.

Flow-related calculations are carried out using the Navier-Stokes Equation. Flow analysis is based on mass conservation and momentum conservation. Because of mass conservation, any change in a given volume's mass over time must be balanced by the flow of an equivalent mass to a corresponding volume. Newton's 2nd law gives that the variation of momentum over time must be equal to the total sum of the forces acting upon the fluid. These two components are combined in the Navier-Stokes Equation.

The calculations were performed using the general purpose commercial numerical analysis software package CFD-ACE.

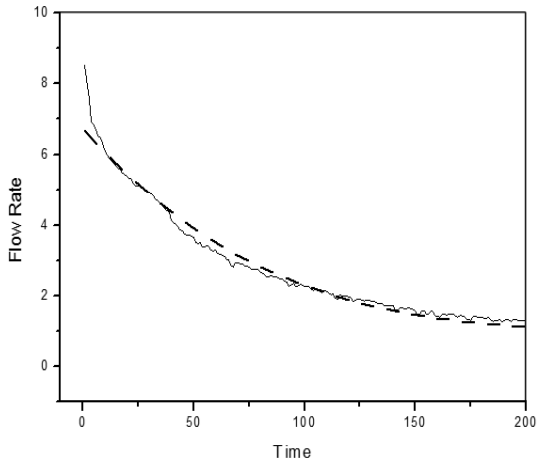


Fig. 3 Average measured flow rate from MH vessel (solid) and 4th-order fit of data (dotted).

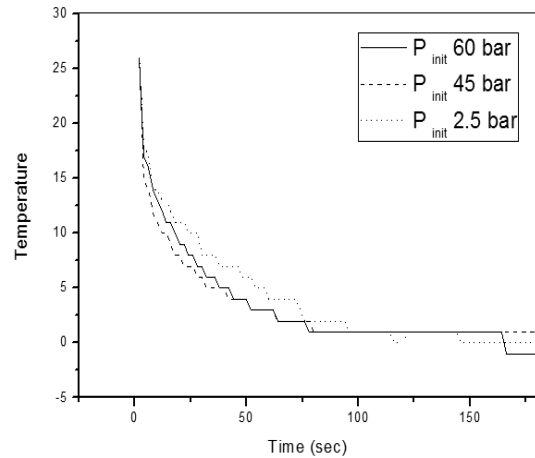


Fig. 4 Measured temperature drop from different initial internal tank pressures.

3. Results and Discussion

3.1 Measured Results

The average measured flow rates upon exposure of the MH device to the atmosphere at 1 atm for 3 minutes (180 seconds) is given as the solid line in Figure 3. The average value is taken from 10 trials.

In the early stages of hydrogen release, the flow rate is relatively high, for three reasons: First, the high concentration of absorbed hydrogen in the alloy results in a greater release of gas. Second, the system's temperature has not yet dropped significantly from the endothermic reaction, which yields a higher flow rate. And third, a significant amount of hydrogen exists within the tank in gaseous form, not reacted with the alloy, and readily escapes the vessel upon opening of the valve.

As the hydrogen release process proceeds, the system's temperature drops and the concentration of hydrogen in the alloy likewise diminishes, resulting in a lower flow rate, which eventually reaches a steady plateau.

3.2 Numerical Model Results

To calculate temperature in the thermal numerical model, the measured flow rate was multiplied by the measured reaction heat value of the alloy, 42 kJ for each mol of hydrogen gas. In the interests of calculation simplicity, a 4th order fit of the average flow data, shown as the dotted line in Figure 3, was used in place of the actual average data. As the figure shows, the deviation between the data fit and the actual data is negligibly small.

A major factor which must be figured into the calculations is the cooling by gas expansion in the experimental system. A significant amount of hydrogen remains in its gaseous form within the vessel, without reacting with the MH alloy. When the vessel is opened to atmospheric pressure, this gas expands rapidly from a compressed state, resulting in a marked decrease of temperature. As the calculations are based on the reaction heat alone, the cooling by gas expansion must be reflected separately in the results.

Figure 4 shows measured temperature changes

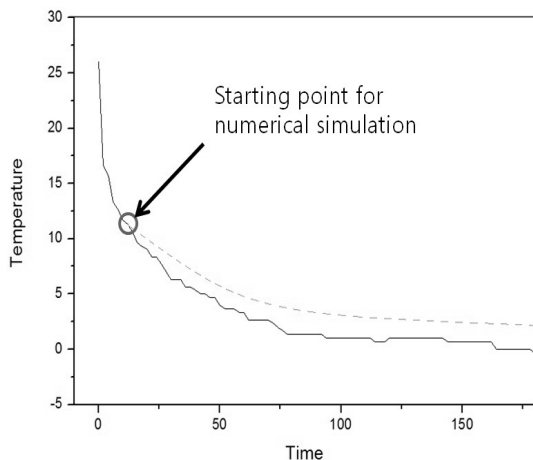


Fig. 5 Measured average temperature (solid) and calculated temperature in MH vessel during hydrogen desorption.

in the center of the vessel for trials beginning from various internal pressure values. While there is some minor deviation between the trials, it appears that the initial steep temperature drop occurs within the first 10 seconds, and for the purposes of this study, this period is assumed to be a period of cooling by gas expansion. Cooling by reaction heat is considered for the period after the initial 10 seconds.

The measured temperature change within the MH hydrogen storage vessel versus the calculated change over the same period is given in Figure 5 as solid and dotted lines, respectively. The initial period of cooling by gas expansion is not reflected in the calculated results. Overall, the trend of decreasing temperature as the endothermic gas desorption reaction progresses is very similar for the measured and calculated results. The minor discrepancies between the values is expected to be an issue caused by assumptions made in the calculations regarding the transition from cooling by gas expansion to cooling by reaction heat.

The calculated results are similar enough to measured values that the numerical model may be

considered reasonably accurate, and may be applied to later studies regarding new system configurations. In particular, the accuracy of temperature prediction from measured reaction rates, or flow rates, will prove useful in the development of a comprehensive numerical reaction model, given further investigation into the relationship between temperature and reaction rates.

4. Conclusions

In this study, we propose a numerical model of the thermal behavior of MH hydrogen storage devices during the discharge of hydrogen gas. An experimental system utilizing kilogram-scale amounts of an alloy with a composition of $Ti_{0.32}Cr_{0.35}V_{0.25}-Fe_{0.08}$ was constructed to obtain bulk-scale data which might be applied to the numerical model. Results show good agreement between the measured and calculated values. The model allows for accurate temperature prediction given reaction rates, and may be further utilized in other systems, and for the development of a comprehensive chemical reaction model.

Acknowledgements

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