

DEVELOPMENT OF A REFERENCE MATERIAL FOR HYDROGEN CONTENTS MEASUREMENT

A. Yun-Hee Lee, B. Yongil Kim, C. Jongseo Park, D. Unbong Baek, and E. Kwon Sang Ryu

Korea Research Institute of Standards and Science (KRISS), Daejeon, Republic of Korea, uni44@kriss.re.kr

Abstract: By heating a metal sample exposed to hydrogen environment until its melting point, whole hydrogen can be released and its content is quantitatively measured with a thermal conductivity detector (TCD). Reference materials with already-known hydrogen contents are needed to calibrate the detector. In this study, we proposed a new concept for making the reference material; the targeted hydrogen content can be obtained by controlling mixing amount of a hydride with its balancing weight. The hydrogen contents can be roughly calculated by considering the chemical stoichiometry of the hydride. A linear proportional relationship was identified between the calculated hydrogen contents and the empirically measured values from the detector. However, both hydrogen contents did not coincide with each other numerically. This phenomenon was discussed from several factors such as partial hydrogenation and air-borne contaminants in the hydride, inconsistent calibration procedure, impurity involved in the measurement, etc.

Keywords: Reference material, Gravimetric hydrogen contents, Thermal hydrogen release, Metal hydride, Hydrogen-assisted damage

1. INTRODUCTION

High-strength steels used in the fields of petro-chemical plants, steel-making facilities, natural gas transmission pipelines, and new energy facilities are often subjected to catastrophic failures [1]. Although these failure phenomena have been generally attributed to hydrogen-assisted cracking (HAC), there is still short of understanding in the failure reasons due to complex interactions among hydrogen atoms, lattice and interface defects, microstructures, internal and external stresses applied to the steel components [2,3].

Anyway the hydrogen contents in steels has been treated as one of detrimental factors causing the hydrogen-induced damages or failures [4,5]. In order to measure the hydrogen contents, a thermal degassing method is suggested; by heating the hydrogen-containing sample until its melting point, the hydrogen atoms located in lattices and trapped in defects are activated and diffuse out from the metallic sample. The released hydrogen can be measured with several detectors such as thermal conductivity cell, pulsed discharge detector, flame ionization detector, etc. Calibration of the detectors is a crucial point for measuring the hydrogen quantitatively. Generally, a hydrogen-charged

metal chip coated with a hydrogen-proof layer is supplied as the reference material (RM). However, the hydrogen content of the commercial RM is limited less than 5 ppm due to the low hydrogen solubility in metals at ambient temperature. In addition, a significant diffusivity of the hydrogen even at room temperature is the another bottleneck for storing the hydrogen reference materials.

Thus, a new concept for fabricating the reference materials was proposed in this study; for achieving higher hydrogen contents in the order of 100 ppm, a metal hydride with a characteristic hydrogen contents was applied as a hydrogen source. Moreover, the thermal stability at ambient temperature is another merit of the metal hydride. By controlling the amounts of the metal hydride and its balancing metal, the aimed hydrogen content could be obtained and confirmed by comparing with an empirically degassed hydrogen amount.

2. EXPERIMENTAL PROCEDURES

The hydrogen source used in this study is a magnesium hydride (MgH_2 , Sigma-Aldrich Co., United States) and its balancing metal was a pure iron (LTS Research Lab., Inc, United States). A 99.99 % pure iron rod was machined into 8 mm beads in diameter. A circular hole having 1 mm diameter was drilled on the bead for charging the metal hydride powder. The iron bead was annealed at 600 °C for 1 h in inert environment in order to remove hydrogen-related impurities and surficial contaminants. Weight of the iron bead was measured using a WX-26 microbalance (Mettler Toledo Int'l Inc., Italy) with a resolution of 1 µg. The microbalance was calibrated with standards weights at the Mass and Related Quantities Laboratory in the KRISS. The hydride powder was carefully encapsulated in the iron bead with a mini-scoop. The hydride-containing iron bead was also weighed with the microbalance to measure the charged hydride weight. Finally the gravimetric hydrogen content of the iron bead was calculated based on the ideal stoichiometry of the magnesium hydride.

In order to confirm the validity of this hydride mixing approach, the hydrogen atoms chemically bonded to magnesium atoms were thermally activated and released from the hydride-charged iron bead using an OH-900 hydrogen determinator (ELTRA GmbH, Germany). The hydride-charged iron bead was dropped into a heat-stabilized carbon crucible. The hydrogen gas released from

the iron bead was quantified by using the thermal conductivity detector installed in the hydrogen determinator.

Chemical composition, phases and de-hydrogenation process of the magnesium hydride were measured using a Dmax 2200 X-ray diffractometer (Rigaku, Japan) and a SDT Q600 thermal gravity analyser (TA Instruments, United States). The X-ray diffraction data were measured over the scattering angle range $5^\circ \leq 2\theta \leq 140^\circ$ at a 2θ step of 0.02° using $\text{CuK}\alpha$ radiation with a graphite monochromator in the reflection geometry at room temperature. The EXPGUI program, which is a graphical user interface for the General Structure Analysis System (GSAS) using the pseudo-Voigt function as a profile function, was used to perform the structural refinement [6,7]. To characterize weight variation of the magnesium hydride by heating, an amount of 6.19 mg MgH_2 powder was loaded on an alumina pan and continuously heated from 298 K to 773 K with the heating rate of 0.17 K/s. An argon gas was supplied with the flow rate of 1.67 mL/s to maintain the inert environment during the heating.

3. RESULTS AND DISCUSSION

Weights measured from the iron beads before and after the hydride charging are summarized in Table 1. Hydrogen content of each bead was calculated by considering the ideal stoichiometry of the MgH_2 . The gravimetric hydrogen content will be 7.66 % if the magnesium hydride has an ideal stoichiometry of MgH_2 ; this theoretical hydrogen contents C_H^{is} can be expressed by W_H divided by $(W_{\text{MH}}+W_B)$, where W_H , W_{MH} and W_B mean the weights of hydrogen, metal hydride and iron bead, respectively. By adding an amount of the metal hydride step-wisely on the iron bead, the hydrogen contents can be controlled from 9.71 to 110.22 ppm.

Table 1. Gravimetric hydrogen contents calculated by assuming the stoichiometric magnesium hydride.

Samples	Bead weight W_B (mg)	MgH_2 weight W_{MH} (mg)	Calculated contents C_H^{is} (ppm)
Bead 1	2006.997	0.262	9.708
Bead 2	2046.087	1.067	45.193
Bead 3	2079.311	1.627	60.278
Bead 4	1940.967	2.533	106.730
Bead 5	2087.440	3.134	110.221

The iron beads charged with the metal hydride artificially were thermally degassed using the OH-900 hydrogen determinator. During the hydrogen releases voltage variations in Fig. 1 were observed and the hydrogen contents were quantitatively measured from the enveloped areas beneath the voltage variation curve. A calibration of the hydrogen determinator was done using a commercial reference material having the nominal hydrogen content of 2.8 ± 0.4 ppm; the integrated area beneath the voltage variation curve from the reference material is measured and

plotted on the Cartesian coordinates having two principal axes of the integrated area and the hydrogen content. A straight calibration line passing two points of the graph origin and the reference hydrogen content is determined for quantitative hydrogen assessments. By inserting the integrated area from each sample in Fig. 1 to the calibration line, the hydrogen content of each iron bead could be measured.

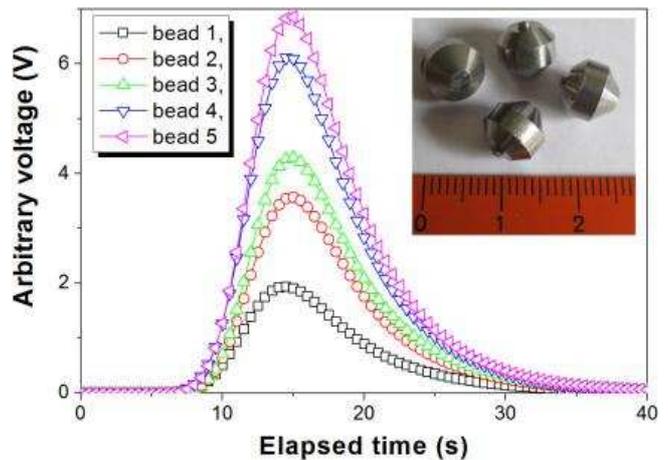


Fig. 1. Voltage variation plots implying hydrogen release from the hydride-charged iron beads.

Both hydrogen contents determined from the theoretical calculation in Table 1 and the empirical degassing data in Fig. 1 are compared in Fig. 2. As might be expected, a linear proportional relationship with the slope of 0.43 was identified between both hydrogen contents. The empirically measured hydrogen contents C_H^{m} were lower than the theoretically calculated values C_H^{is} . This phenomenon can be simply explained with the stoichiometry of a metal hydride. An actual composition of the metal hydride can be expressed by MgH_{2-x} and a previous study [8] proposes a post-hydrogenation process for reducing the hydrogen deficient x .

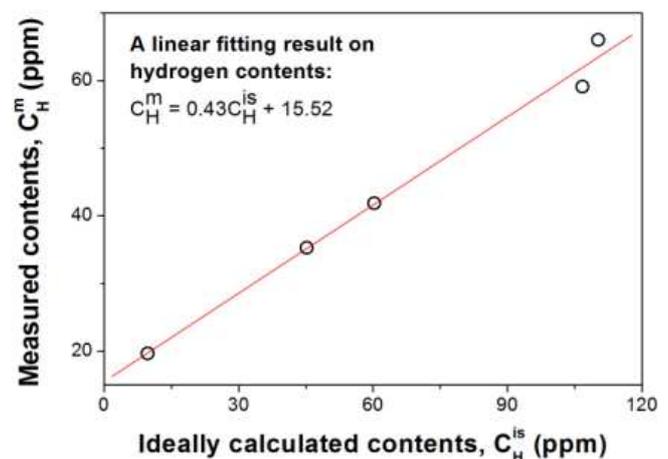


Fig. 2. Comparison of the hydrogen contents determined from the theoretical calculation and the thermal degassing measurement.

To characterize the chemical composition of the MgH_2 powder, the X-ray diffraction patterns were measured and

plotted in Fig. 3. Plus marks (+) representing the observed intensities are overlapped with the calculated solid line. All reflection peaks of the MgH_2 powder whose locations were marked with ticks in Fig. 3 were indexed via the Pawley refinement using the lattice parameters and the space group for the tetragonal crystal system with the space group $P4_2/mnm$. The Pawley refinement showed that the lattice parameters of MgH_2 were $a(\text{or } b)=4.5200(2)$ and $c=3.0229(2)$ Å. Peaks corresponding to the non-hydrogenated Mg were also measured and their locations were marked with triangles in Fig. 3. More complicated peaks indicated with arrows in Fig. 3 are ascribed to different hydride phases under high pressures, magnesium oxide, and other unknown contaminants. Thus, it was impossible to determine the compositional deficiency x from Fig. 3.

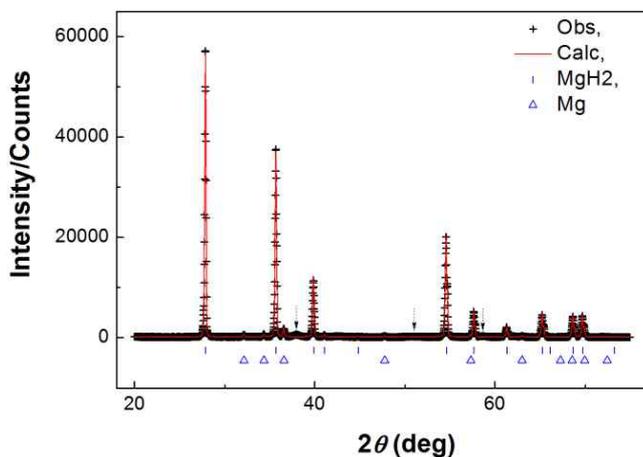


Fig. 3. Structural refinement patterns of MgH_2 using X-ray powder diffraction data at ambient temperature.

Regardless of the complex mixture of different phases and contaminants, the most important information to be determined is an actual amount of hydrogen release during the thermal degassing. Thus, the thermal gravity analysis (TGA) combined with the differential scanning calorimetry (DSC) was carried out for the MgH_2 powder. Weight variation of the sample was profiled with temperature increment and the calorimetric heat flow during the heating was also overlapped in Fig. 4. A continuous weight loss occurred around 500 K and this is attributed to the dehydration of the hydroxide which can be formed when a metal hydride is exposed to air. A metal hydride can easily react with the moisture in air and forms hydroxides. This dehydration did not form any significant peak in the DSC curve. While a significant phase transformation attributed to the de-hydrogenation started at 699 K and heat flow for the transformation was estimated by 2.65 kJ/g from the DSC curve. The weight gain after the de-hydrogenation may be explained with subsequent oxidation of the formed magnesium. As the result, weight losses of the magnesium hydride can be explained with two causes of dehydration and hydrogen release. Thus, the portion of the hydrogen release in the whole weight loss must be considered to calculate the actual hydrogen contents. The portion of the hydrogen release was 0.75 of the whole weight loss and the

actual hydrogen contents were re-calculated by multiplying this value to the ideal hydrogen contents in Table 1.

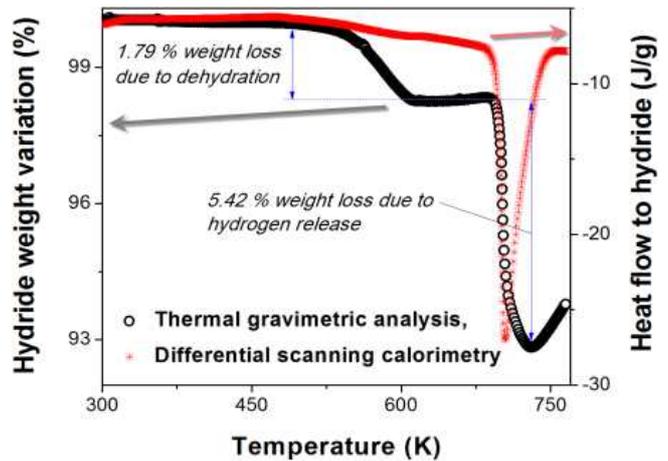


Fig. 4. Weight variation and heat flow related to the thermal de-hydrogenation of the MgH_2 powder.

The re-calculated hydrogen contents C_H^{ec} based on the thermal gravimetric analysis are compared with the empirically measured results C_H^{m} with the OH-900 hydrogen determinator. A linear-proportional relationship was maintained between both hydrogen contents. However, the proportional slope was 0.61, more close to the unity. The intercept of the linear fitting was 16.33; this means that the thermal degassing method has a background content of hydrogen which can be originated from carbon crucible, impurities in carrier gas, etc. To identify the background hydrogen content, a thermal degassing measurement was carried out without a specimen drop. However any hydrogen was not detected from the environmental experiment. If the reference material works ideally, the calculated hydrogen contents will exactly correspond to the empirically degassed values. It means that the corresponding linear fitting must have its slope of unity and pass through the graph origin.

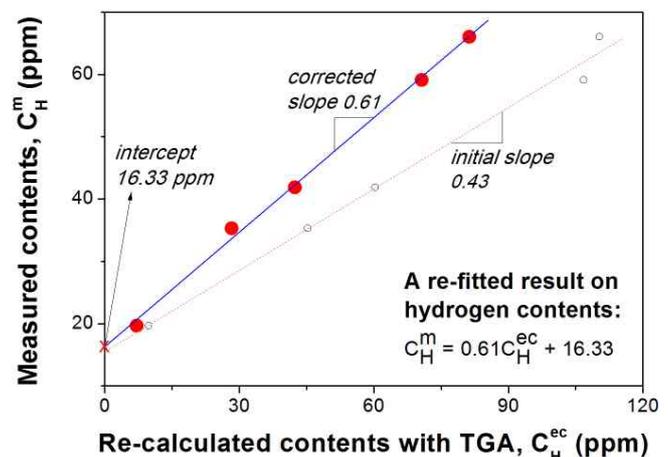


Fig. 5. Comparison of the hydrogen contents determined from the re-calculation based on the hydrogen release portion and the thermal degassing measurement.

The differences in the fitting slope and the intercept with those of the ideal case can be explained with an inconsistent calibration or a systematic error from the OH-900 hydrogen

determinator [9]. In this study, the hydrogen determinator was calibrated with one reference material having the hydrogen contents of 2.8 ± 0.4 ppm. Even though the hydrogen contents are properly determined for the commercial reference material with dilute hydrogen contents, it is very difficult to extrapolate this reference value to higher hydrogen contents in 100 ppm. This one-point calibration can bring about a risk of overestimation or underestimation in the hydrogen measurements. If the calibration line used in this study has a lower slope than that of the normal calibration line due to the hydrogen underestimates from the commercial reference material, the whole measured contents C_H^m in Figs. 2 and 5 can be underestimated. If the calibration line is properly corrected, the measured hydrogen contents C_H^m will increase proportionally and finally will form the fitting slope approaching 1.0. The intercept deviation of the origin can be easily explained by the impurities in crucible, carrier gas and other testing environments. However, the dummy measurement without any specimen results in no background or baseline hydrogen contents. Thus an existence of the intercept value cannot be clearly explained at this research step. This might be related to the calibration procedure and also the contaminants in the hydride shown in Figs. 3 and 4. Environment-controlled measurements are scheduled and these will explain the background hydrogen contents and the calibration results.

4. CONCLUSIONS

A determination of the hydrogen contents in a metal sample is the first step for studying the hydrogen-induced damages and failures. A new concept for making reference materials necessary for quantitative hydrogen measurements is proposed in this study; a hydride charged iron bead was fabricated and its hydrogen content in ppm level could be artificially controlled by varying mixing amount of the hydride. The theoretically calculated hydrogen contents showed a linear proportional relationship with the empirically released values. In order to explain the discrepancies in both hydrogen contents in numerical values, an X-ray diffraction and a thermal gravity analysis were performed with the magnesium hydride. From the results, the actual hydrogen contents were re-calculated and compared with the empirically measured values. The re-calculations resulted in a clear one-to-one relationship with the measured hydrogen contents. However, both hydrogen contents do not agree each other numerically. This phenomenon was discussed from the inconsistent calibration of the hydrogen determinator, air-borne contaminants in the hydride and impurities involved in the measurements. Through environment-controlled measurements, these issues are expected to be clearly explained at the next research step.

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