

# Doctoral Thesis

## Research and development of hydrogen chemical compressor using hydrogen storage alloys (Digest)

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## 学位論文の要旨

論文題目            Research and development of hydrogen chemical compressor using hydrogen storage alloys

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### 論文の要旨

The hydrogen energy society refers to a sustainable society by building an appropriate social infrastructure for hydrogen. Because the requirement to reduce the CO<sub>2</sub> emission is quite strict, energy resources should be shifted from the fossil fuel as the current major resources to renewable energy resources, like solar, hydro wind and so on. However, these renewable energies are quite fluctuated and localized at a specific area. So, hydrogen as the energy carrier of the renewable energies should be utilized. When hydrogen is used as the energy carrier, there are four phases of “generation”, “boosting”, “storage” and “utilization”, and it is necessary to construct optimal social infrastructure for each. For building these hydrogen infrastructures, various researches, including hydrogen storage alloys, are being conducted.

Hydrogen storage alloys are metallic materials that can store hydrogen gas by forming metal hydride through chemical reaction between the metal and hydrogen, which have been investigated as hydrogen source for fuel cell vehicles, as well as various applications such as, actuators, chemical heat pumps, and nickel-metal hydride batteries. It is known that hydrogen absorption/desorption reactions of the hydrogen storage alloy can be controlled by the temperature and/or hydrogen pressure of the alloy. Hydrogen absorption/desorption pressure is increased exponentially with temperature, showing the Arrhenius type behaviour. Using this property, one can compress hydrogen thermochemically by a high temperature enough to be obtained from the waste heat. In other words, hydrogen storage alloys can absorb low-pressure hydrogen at low temperature, and then, can desorb high-pressure hydrogen at high

temperature by heating the alloys.

In Japan, studies of the hydrogen storage alloys have been conducted as a hydrogen storage material for mobile application (e.g. vehicles) so far. For that reason, the study has been more focused on improving hydrogen storage capacity per weight and weight reduction. However, if we use hydrogen storage alloys as a stationary application, weight reduction is no longer an issue to be solved. Therefore, hydrogen storage alloys began to be re-expected as chemical compressor and high pressure hydrogen gas tank. In this case, the temperature dependence of the hydrogen plateau pressure is more important for their practical application. By using the hydrogen storage alloys that have not been studied so far in details, it may be possible to design a desirable chemical compressor. Furthermore, by using the hydrogen storage alloys with hydrogen desorption temperature of 200 °C or less, it would be possible to utilize a lower heat source that is usually discarded without use; e.g., waste heat from solar thermal power plants, factories or refuse incineration plants.

As a device that uses hydrogen as a fuel, FCV is mostly promising. In order to increase the number of FCVs, the number of the hydrogen filling station should be increased more and more with low cost, convenience, and multiscale. In order to overcome these requirements, the chemical compressor using hydrogen storage alloy is likely to be used as one of the best social infrastructures.

To design a chemical compressor up to 82 MPa for a hydrogen station, following studies were carried out in this thesis.

(1) Design and demonstration of prototype of chemical compressor using hydrogen storage alloys is described in chapter 4. The author brought the prototype to Hydrogen Energy Test and Research Center (HyTReC) and examined that it can boost up to around 80 MPa by heat. Some chemical compressors using hydrogen storage alloys are commercialized in foreign countries, but there are few examples demonstrating 80 MPa classes for hydrogen station. By this approach, it is possible to confirm the feasibility of hydrogen boosting using hydrogen storage alloys for hydrogen station.

(2)  $Ti_{1.1}CrMn$  is one of potential hydrogen storage alloys used on the second stage of chemical compressor. Characteristics of  $Ti_{1.1}CrMn$  at high temperature and high pressure region were investigated and described in chapter 5.

(3) Optimum design of chemical compressor for small hydrogen station was described in chapter 6. Considering advanced design by CAE software and characteristics of the hydrogen storage alloy described in chapter 5, The author studied a chemical compressor with discharge capacity of  $30 \text{ Nm}^3/\text{h}$ . As one of the advantages of a chemical compressors using hydrogen storage alloys, high pressure hydrogen gas storage tanks may be unnecessary. Therefore, the author examined the two filling methods; direct filling from the chemical compressor without the high pressure gas tank and differential pressure filling with the high pressure gas tank.

As one of important conclusion, hydrogen desorption isobar of  $Ti_{1.1}CrMn$  at 82 MPa was investigated. From the obtained isobar plot, one can know the required temperature for hydrogen release at 82 MPa depending on hydrogen content in the  $Ti_{1.1}CrMn$  alloy. And it is possible to optimally design thermochemical hydrogen compressor, depending on the temperature of the waste heat available from the surrounding environment and the required compression ability.

Moreover, assuming that a small hydrogen station is constructed in a place where hydrogen is generated and waste heat exists nearby, a chemical compressor with discharge capacity of  $30 \text{ Nm}^3/\text{h}$  which is one tenth of the current  $340 \text{ Nm}^3/\text{h}$  is required at this small hydrogen station, and the optimum design of this chemical compressor was examined. Finally, a chemical compressor was designed with 12 low pressure reactors made of SUS316, 20 high pressure reactors made of CDA17200 (copper beryllium alloy), and 2704 kg of Ti-Cr alloy. By circulating the heating medium at  $220 \text{ }^\circ\text{C}$ , necessary heat exchange is able to be completed within the target time.

In the future, in order to advance the design, it is necessary to study temperature decreasing and hydrogen absorption, which is more difficult than temperature rising and hydrogen desorption. Furthermore, it is necessary to obtain

knowledge using a larger demonstration machine or a commercialized product and examine more optimum design and operation.

## 論文目録

氏名 鶴井 宣仁

### 学位論文

論文題目 Research and development of hydrogen chemical compressor using hydrogen storage alloys (水素吸蔵合金を用いた水素昇圧システムの研究開発)

公表の方法 広島大学学術情報リポジトリで全文を公表するほか、広島大学大学院総合科学研究科紀要に要旨を公表し、次のとおり分割して公表する。

第1章 関係論文の1

第5章 関係論文の2 (2018年1月金属学会誌に投稿)

### 参考論文

#### I 関係論文

1 著者名：鶴井宣仁, 市川貴之

論文題目：水素吸蔵合金を用いた水素昇圧システム

著書名：小島由継監修『水素貯蔵材料の開発と応用』

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2 著者名：Nobuhito Tsurui, Kiyotaka Goshoume, Satoshi Hino, Tetsuhiko Maeda, Hiroki Miyaoka, and Takayuki Ichikawa

論文題目：Hydrogen isobar properties of  $Ti_{1.1}CrMn$  in high temperature and high pressure region (高温高圧域における  $Ti_{1.1}CrMn$  の水素放出等圧特性)

雑誌名：MATERIALS TRANSACTIONS (査読制度あり, 2018年1月投稿, 2月受理予定)

#### II その他

なし