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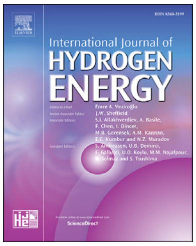

Simulation and design of a three-stage metal hydride hydrogen compressor based on experimental thermodynamic data

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ABSTRACT

A semi-empirical method was developed to design a three stage Metal Hydride Hydrogen Compressor (MHHC) through the determination of thermodynamic properties of several hydrides. As a first step, three AB_2-type alloys that satisfy operation conditions were selected from published thermodynamic data entailing over 200 single plateau hydrides. These alloys were synthetized by arc melting and characterized by X-Ray Powder Diffraction (XRPD), Scanning Electron Microscopy (SEM) and Energy Dispersion X-ray spectroscopy (EDX). Absorption and desorption Pressure-composition-Isotherms (P-c-I) were determined between 23 and 80 °C to characterize their thermodynamic properties. Subsequently, an algorithm that uses these experimental data and a real equation of state for gaseous H_2 was implemented to simulate the volume, alloy mass, pressure and temperature of operation for each compressor stage, while optimizing the compression ratio and total number of compressed H_2 moles. Optimal desorption temperatures for the three stages were identified within the range of 110–132 °C. A system compression ratio (CR) of 92 was achieved. The number of H_2 moles compressed, the alloy mass and volume of each stage depend linearly on the volume of the external tank in which the hydrogen is delivered.

Introduction

The urgency to replace fossil fuels by sustainable renewable ones has increased the research on novel technologies. Between several choices, hydrogen excels as an energy vector that can help to reduce greenhouse gases thanks to its high energy content and diversified sources of supply [1,2]. Key features in the hydrogen cycle are its production, transport and storage [3,4]. On this regard, hydrogen compressors provide an excellent approach to integrate the production and storage with the distribution of hydrogen as an energy carrier for different applications [5–7]. Specifically, Metal Hydride Hydrogen Compressors (MHHC) give great improvements in comparison to other compression technologies and therefore have focused much attention in recent years [5,6].

Several approaches have been followed to enhance MHHC performances [5]. Simulations are particularly useful to

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predict and design hydrogen sorption and thermal management in Metal Hydride (MH) tanks, including MHHC. Hardy et al. [8] developed a hierarchical methodology for modeling hydrogen storage systems, in which a finite element method (FEM) were used to simulate and optimize the hydrogen sorption properties of a cylindrical hydrogen storage tank containing sodium alanate with a shell and tube type heat exchanger. Although the model gave proper results, some realistic features such as hysteresis and the volume expansion of the complex hydride during sorption were not taken into account and the system geometry required further optimization. Førde et al. [9] developed a one-dimensional heat and mass transfer model with an ideal equation of state (EOS) for a MH-based hydrogen storage system. It was validated with experimental results from a $La_{0.83}Ce_{0.10}Pr_{0.04}Nd_{0.03}Ni_{4.4}Al_{0.60}$ alloy at different temperatures and hydrogenation pressures. This model exhibited a higher sensitivity to kinetic and thermal parameters such as the activation energy, effective thermal conductivity and heat of the reaction than with other operational variables described. Gkanas et al. [10] optimized the compression ratio by combining hydride materials AB_5 ($LaNi_5$ and $MmNi_{4.6}Al_{0.4}$) and AB_2 (Zr–V–Mn–Nb and Ti–Zr–V–Fe–Cr–Mn) for the first and second stage of the compressor, while maximizing the hydrogen rate using numerical simulations to predict the real behavior of the system.

Moreover, some prototypes and experimental approaches have been developed. Laurencelle et al. [11], designed a three-stage AB_5 MHHC prototype for a hydrogen production facility using a low-pressure alkaline electrolyzer. The materials selected for the system were $LaNi_{4.8}Sn_{0.2}$, $LaNi_5$ and $MmNi_{4.7}Al_{0.3}$ for the first, second and third stage respectively, where it performs a thermal cycling between 20 and 80 °C with a flow rate that reaches about 20 L (NTP) of hydrogen per hour. Vanhanen et al. [12] studied the feasibility of combined MHHC and heat pump through the characterization of various alloys. The alloys used for both compression and heat pump were the Hydralloy C2 and Hydralloy C0 for the first and second stage, respectively. Although, if a third alloy ($TiCrMn_{0.55}Fe_{0.33}V_{0.15}$) was added, the hydrogen pressure increased from 12 to 18 bar up to 85–110 bar by utilizing a very narrow temperature interval (20-60 °C),then the hydrogen pressure could reach almost 199 bar. As a result, a three stage MHHC gave greater results than just a two stage one. Wang et al. [13] developed a two-stage 700 bar hydride compressor using AB_2 hydrides by comparing the thermodynamic behavior of different compositions of the AB_2 alloys Ti–Cr–Mn and Ti–Zr–Cr–Fe–V, for the first and second stage of the compressor respectively. With exchanging cold oil (298 K) and hot oil (423 K), the built compression system could convert hydrogen pressure from around 40 bar to over 700 bar. Lototsky et al. [14] created a prototype MH compressor operating in a temperature range 20–150 °C and providing compression of hydrogen from 10 to 200 bar with an average productivity up to 1 m^3/h. The compressor has a two stage layout where the first part uses AB_5- and the second AB_2-type hydride-forming intermetallic compounds. Bhuiya et al. [15] made an experiment-driven design procedure in order to optimize the parameters between stages in a dual-stage hydrogen compressor and subsequently achieved an enhanced compression ratio. The compressor system was composed by a $LaNi_5$ in the first stage and a $Ca_{0.2}Mm_{0.8}Ni_5$ in the second one, obtaining a higher couple compression ratio (53%) than the one acquired with just the hydride of the first stage. Muthukumar et al. [16] performed experimental tests on a $MmNi_{4.6}Al_{0.4}$ based hydrogen compressor by varying operating parameters such as supply pressure and heating temperature under constant and variable delivery pressures with different storage volumes. Hydrogen storage pressure increases with a rise in the supply pressure and heating temperature. In the best conditions studied, with a variable H_2 delivery a maximum isentropic efficiency of 7.3% is obtained at a CR of 8.8 (43.8/5 bar) and 95 °C hot fluid temperature, while with a constant delivery, the corresponding efficiency is 14.2%, the CR is 3 (30/10 bar) and the hot fluid is at 85 °C. To summarize, previous studies are focused in the best combination of alloys at different stages of compression while searching the enhancement of the kinetics through geometry optimization.

Unfortunately, several MHHC works disregard many important thermodynamic features such as sloping plateau and hysteresis during the metal-hydrogen reaction or the use of real H_2 equation of state (EOS). Moreover, they only considered the combination of a few materials, though the thermodynamics of many MH are reported in the literature [5,17]. On this regard, Voskuilen et al. [18] developed an interesting approach by creating a fairly conscious data base of MH and the use of a simple numerical model to select a combination of materials for a two-hydride thermal system, specifically a heat pump. Thermophysical and kinetic properties of the alloys selected were considered to optimize a key system parameter like the Coefficient of Performance (COP).

The novelty of the present work is twofold. Firstly, the implementation of more than 200 alloys for a selection program, aids to ensure that the materials selected are an optimum combination for MHHC design. Secondly, real H_2 gas EOS as well as experimental features of the alloys (*i.e.* sloping plateau, hysteresis, and variation of the reversible capacity with temperature) were considered to account for the real behavior of these materials and their combined influence in the final outcome of the system.

As a result, a new methodology is developed for improving the selection of materials for a MHHC system and, therefore, its performance. In the first part of the study, thermophysical data from literature and operational parameters of the compressor are considered to select the proper materials trough a simple model based on ideal thermodynamics. Then, the selected materials were synthesized and characterized chemically, structurally and thermodynamically. Finally, an algorithm that considers the realistic thermodynamic models and real gas H_2 EOS is implemented to define and optimize some parameters of the MHHC system (*i.e.*, volume and alloy mass of each stage) to deliver the greatest quantity of hydrogen compressed at the highest compression ratio.

Materials and methodology

First of all, the thermophysical properties of more than 200 alloys from a data base [18] and literature studies [19–39] were considered to implement a selection program for a three-stage MHHC. The operational parameters of the system were