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Magnetic refrigerator for hydrogen liquefaction

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ABSTRACT

This paper reviews the status of magnetic refrigeration system for hydrogen liquefaction. There is no doubt that hydrogen is one of most important energy sources in the near future. In particular, liquid hydrogen can be utilized for infrastructure construction consisting of storage and transportation. When we compare the consuming energy of hydrogen liquefaction with high pressurized hydrogen gas, FOM must be larger than 0.57 for hydrogen liquefaction. Thus, we need to develop a highly efficient liquefaction method. Magnetic refrigeration using the magneto-caloric effect has potential to realize not only the higher liquefaction efficiency >50%, but also to be environmentally friendly and cost effective. Our hydrogen magnetic refrigeration system consists of Carnot cycle for liquefaction stage and AMR (active magnetic regenerator) cycle for precooling stages. For the Carnot cycle, we develop the high efficient system with >80% liquefaction efficiency by using the heat pipe. For the AMR cycle, we studied two kinds of displacer systems, which transferred the working fluid. We confirmed the AMR effect with the cooling temperature span of 12 K for 1.8 T of the magnetic field and 6 s of the cycle. By using the simulation, we estimate the efficiency of the hydrogen liquefaction plant for 10 kg/day. A FOM of 0.47 is obtained for operation temperature between 20 K and 77 K including LN_2 work input.

1. Introduction

Hydrogen has been considered as one of the cleanest energy resources and also useful cold refrigerant for superconducting technologies operating >20 K. Using hydrogen in our society requires the infrastructure construction consisting of hydrogen generation, liquefaction, storage and transportation. Liquid hydrogen has a higher density than that of gaseous one, so it is great advantage for storage and transportation. However, liquid hydrogen has a cryogenic temperature ∼20 K, so we must realize highly efficient liquefaction methods and adiabatic storage with safety.

There are many hydrogen liquefaction plants and they have achieved quite high FOM (=figure of merit) as much as ∼0.4, but this value is not enough to use for the hydrogen applications at room temperatures. When we compare the consuming energy of hydrogen liquefaction with high pressurized hydrogen gas (typically 70 MPa), the FOM must be larger than 0.57 for hydrogen liquefaction to require less energy [1]. This is the reason why we need to develop more efficient refrigeration system for hydrogen liquefaction.

Magnetic refrigeration method makes use of the magnetocaloric effect (MCE) where some magnetic materials exhaust or absorb heat by applying or removing external magnetic fields. MCE is induced by the internal magnetic entropy change of magnetic materials and it occurs through the magnetic material with a lighting speed, thus magnetic refrigeration can operate an ideal cycle like Carnot. Another advantage of magnetic refrigeration is to use the solid magnetic materials, which have typically 1000 times higher entropy density than that of gas. Magnetic refrigeration systems can be environmentally friendly, quiet operation and possibly more efficient than conventional liquefaction methods.

In this review paper, we will describe the experimental system for Carnot and AMR cycles with magnetic materials and magnet. Also some simulation results for the whole refrigeration system will be shown to predict the future development of hydrogen magnetic refrigeration.

2. Scheme of hydrogen magnetic refrigeration cycle

To realize a hydrogen liquefaction cycle by using a magnetic refrigerator, we need several cascaded cycles to cover wide temperature ranges from heat source temperatures to liquid hydrogen temperature (20.3 K). The source temperature is usually set at

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room temperature, but we also can consider the use of liquid natural gas = LNG (112 K) or liquid hydrogen (77 K) for connecting to the magnetic refrigerator. This is because a number of LNG plants have been built in Japan for the energy source and LNG also can be used as a hydrogen source. Since the temperature of LNG is already cold, LNG will contribute largely to improve the efficiency of the hydrogen magnetic refrigerator cycle [2].

Fig. 1 shows a typical gas flow circuit of the hydrogen liquefaction cycle of the magnetic refrigeration. There are two kinds of magnetic refrigeration cycles; CMR = Carnot Magnetic Refrigerator and AMR = Active Magnetic Refrigerator. Hydrogen gas is pre-cooled to the temperature slightly above the boiling point with an AMR, and then it is liquefied with a CMR. Since the CMR provides a temperature span of a few degrees, another AMR must be connected to the CMR to absorb the exhausted heat. AMR can provide large refrigeration temperature span, but usually we need to cascade several units of AMR to reach ~22 K.

3. Carnot cycle for liquefaction stage

3.1. Liquefaction principal

For the liquefaction stage by the CMR, we use a heat pipe to condense the hydrogen gas by the magnetic material. This method achieves considerably higher thermal efficiency compared with the conventional method using the Joule–Thomson valve. Fig. 2 shows how hydrogen gas is condensed directly on the surface of the magnetic materials, subsequently liquid hydrogen drops downwards to a reservoir. The principal is equivalent to a thermo-siphon, a type of a heat pipe, and categorized into the heat transport regime making use of gravity unlike the normal thermo-siphon uses capillary phenomena for liquid circulation. This method makes use of the phase transition from gas to liquid and therefore, it's coefficient of overall heat transfer is highly comparable to that of copper material.

3.2. Experimental system

Fig. 3 shows CMR test apparatus consisting of magnetic refrigerant, a 6 T superconducting magnet and a heat switch [3]. The magnetic field applied on the magnetic refrigerant is varied by moving the refrigerant (0.28 kg of dysprosium gadolinium aluminum garnet, DGAG) by 15 cm in the magnet with a drive shaft connected to a displacer. Since the superconducting magnet is a solenoid type of a magnet without a bucking coil, the magnetic

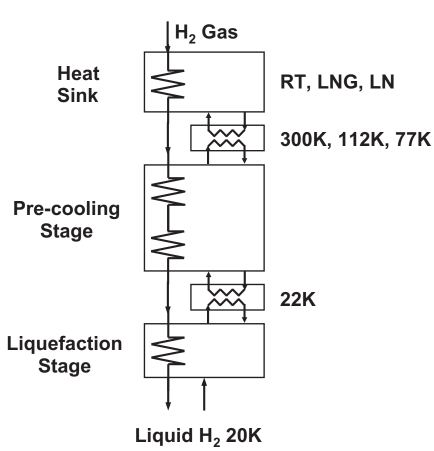

Fig. 1. Hydrogen gas flow circuit of hydrogen liquefaction cycle for the magnetic refrigeration, consisting of CMR and AMR.

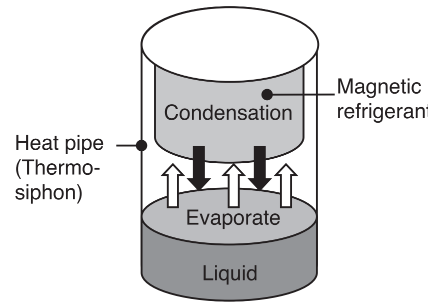

Fig. 2. Liquefaction principal of magnetic refrigerator based on thermo-siphon method.

field only reduces to 1 T at 15 cm away from the magnet center. However, DGAG exhibits large entropy change at higher magnetic field, therefore the impact of a non-zero low field is reduced.

In Fig. 3, at the start of the cooling cycle, DGAG, initially at the center of the magnet, starts to move downwards to a shaded area called a liquefaction stage decreasing its temperature by the magnetocaloric effect. Hydrogen gas filling the liquefaction stage starts liquefying when DGAG temperature dips from the liquefaction temperature. After a certain period, DGAG starts to move back to the original magnet center increasing its temperature. Heat from DGAG is transferred at the magnet center with a gas-gap heat switch connected to a conventional G–M mechanical cryocooler. For our refrigerator, the operation frequency is adjustable from 0.01 Hz to 0.5 Hz, which is mostly limited by the heat transfer rate of 5–10 W/K in the gas-gap heat switch.

3.3. Magnetic materials

In general, rare-earth metallic compounds such as $ErAl_2$ provide large entropy changes in the temperature range of 20–77 K, but these materials easily absorb hydrogen. Usually this kind of phenomena causes the materials to decompose to powders. For the liquefaction process, the best way is to condense the hydrogen gas directly on the surface of the magnetic material, so we need to develop the materials that do not decompose. For this reason, we developed a ceramic magnetic refrigerant, dysprosium gadolinium aluminum garnet, DGAG to avoid this difficulty [3]. The reason why Gd is added is that garnets including Gd tend to increases the zero magnetic field entropy because of the large magnetic moment of the Gd ion; $J = 7/2$. Gadolinium ion is generally localized in the garnet crystal structure due to no spin–orbital coupling, and therefore, a large magnetic moment can be held even in low temperatures. Fig. 4 shows the entropy diagram for poly crystal 20%DGAG = $Dy_{2.4}Gd_{0.6}Al_5O_{12}$.

In order to maximize the surface area of DGAG and to flow hydrogen gas without large pressure loss, DGAG is formed in platy shape as seen in Fig. 5. Thus, the whole DGAG holder consists of a copper hollow cylinder with slits and rectangular solid DGAGs line up in parallel to each other with a gap of 1 mm. The holder is also placed in parallel to hydrogen flow direction.

3.4. Experimental results

In our experiments, hydrogen liquefaction is judged from the temperature variation with thermometers on DGAG due to lack of an appropriate commercial level detector that can be used in our small experimental cell [3,4]. A tiny thermometer (CERNOX CX-SD) was set on the surface of the DGAG plate by using varnish (GE 7031). The measurement point was close to center of the sample holder. Total mass of the DGAG was 269 g and filling factor was 0.34.