DISPROPORTIONATION RESISTANT ALLOY DEVELOPMENT FOR HYDRIDE HYDROGEN COMPRESSION

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Abstract

Ergenics, Inc. has been supplying metal hydride hydrogen compressors for twenty years. The hydride compressor is an absorption-based system that uses the properties of reversible metal hydride alloys to silently and cleanly compress hydrogen; hydrogen is absorbed into an alloy bed at ambient temperature and, subsequently, is released at elevated pressure when the bed is heated. Compression energy can be supplied by hot water or electrical resistance heat. The primary technical objective of this project is to determine whether hydride compressors can be used for non-pure hydrogen streams likely to result from advanced hydrogen production methods (i.e. from renewable resources), with the commercial objective of developing a viable hydride compressor that offers substantial benefits over mechanical compressors. Cost effective operating efficiency is a necessary element of the commercial objective .

One way to increase hydride compressor efficiency is to increase the operating temperature of the heating cycle. Traditional hydride alloys tend to degrade from a phenomenon termed disproportionation when cycled at temperatures above 100°C. To assure long term reliable operation, Ergenics developed proprietary hydride alloys that resist disproportionation in the compression environment. This paper summarizes work on high temperature alloy development.

Introduction

Ergenics is investigating the application of its novel hydride hydrogen compression process to hydrogen produced from renewable resources (DaCosta 2000). Thermal hydrogen compressors have offered significant operational and economic advantages over traditional mechanical compressors when the hydrogen is pure and flow rates are relatively low. However, hydrogen produced from renewable resources can contain impurities that might damage a hydride compressor and, if hydride compressors are to play a major role as hydrogen becomes an increasingly important part of America's energy supply, increased flow rate capabilities must be economical. In addition, new storage systems require hydrogen pressures of 5,000 to 10,000 psig, much higher than the current industrial practice of 3,600 psig.

In work reported last year (Golben & DaCosta 2001), Ergenics demonstrated hydride compressor operation at an outlet pressure of over 5,000 psig. Hydride alloy tolerance to impurities and the use of miniature, modular hydride heat exchangers to economically achieve higher flow rates will be investigated and demonstrated by Ergenics in the second half of the year 2002.

One element important to hydride compressor commercial viability is operating efficiency. The ability to compress hydrogen using the low-grade heat energy in hot water is a compelling advantage of the thermal compression process. However, many applications either do not have adequate waste heat, or the waste heat is difficult to access economically. In these cases, traditional fuels can be used to provide compression energy, but the relatively low operating efficiency of the hydride compression process must be increased.

Ergenics has developed a compression cycle that can use traditional fuels and can reduce compression energy cost to less than one half of that required for a mechanical compressor. A new class of hydride alloys that will work in these applications have been identified.

Hydride Compressor Efficiency

The hydride compressor is a form of "heat engine" based on the Carnot cycle. Its energy efficiency is about 50% of Carnot efficiency. Carnot efficiency is based on the temperature difference between the hot energy source and the cold heat sink. Efficiency plotted as a function of hot water (energy source) temperature appears in Figure 1.

Waste heat is usually available in the 80 to 90°C range. With a 30°C cooling water temperature, Carnot efficiency is from 13 to 16 percent and hydride compressor efficiency is from 4½ to 6½ percent. If waste heat is free, cycle economics can endure this level of efficiency.

By using a traditional form of heat energy, such as natural gas, cycle economics will benefit from an increase in hot water temperature. Using a heat transfer fluid from a gas fired heater at 130°C, Carnot efficiency is almost 25 percent, and hydride compressor efficiency increases to 15 percent. While 15 percent is about 1/2 that for a mechanical compressor, electricity is about 6 times costlier than natural gas, so the hydride compressor will enjoy a 67% lower energy cost.

An added benefit of higher temperature operation is a substantial reduction in the number of stages needed for a given compression ratio. Operation at 130°C in lieu of 90°C cuts by half the number of stages, with an associated reduction in system complexity, size and capital cost.

High Temperature Reversible Metal Hydride Alloys

Hydride alloys traditionally used for compressors have been from the "AB_5" family.[1] AB_5 alloys have good capacity, usually storing from 1% to 1.3% hydrogen by weight. They can operate for over a million cycles at temperatures from ambient up to a little over 100°C.

1 - Hydrides are often described in terms of a chemical formula as A_XB_Y, where the A signifies an element that reacts with hydrogen to form a hydride and B signifies an element that modifies the conditions under which the reaction takes place. Often tertiary additions are made to the A and/or B sides to achieve a desired performance. Most hydride alloys are members of the following families: AB, A_2B, AB_2, and AB_5.

When these alloys are cycled at higher temperatures and elevated pressures, their performance can deteriorate through a process termed "disproportionation." In relatively few cycles, reversible hydrogen absorption capacity is lost, which would cause a hydride compressor to stop working.

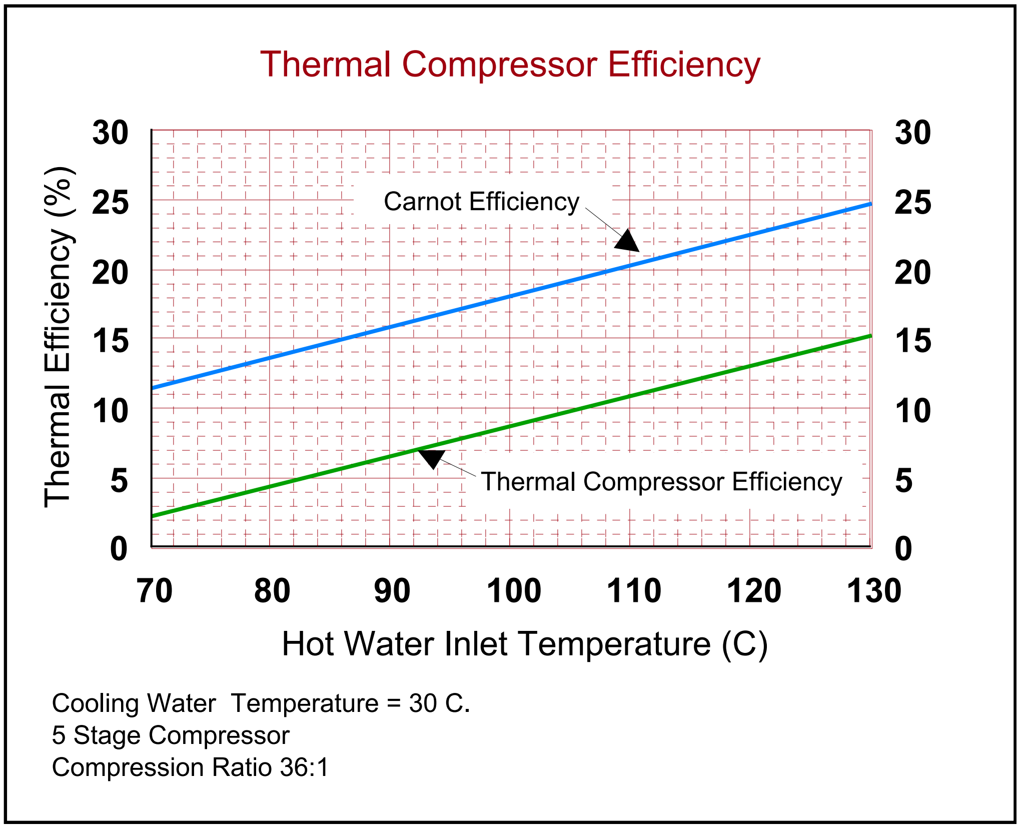

Figure 1 - Hydride "thermal" compressor operating efficiency is about 50% of Carnot efficiency.

Ergenics pioneered the development of high temperature, disproportionation resistant alloys in 1995, while applying a hydride heat storage system to heat an automotive catalytic converter when the car was started. A hydride heater bed was placed in the exhaust pipe between the exhaust manifold and the catalytic converter. When activated, the heater bed temperature would increase from ambient to 400°C in a few seconds. The bed would be heated to over 500°C during normal driving.

The original AB alloy used for the hot heat exchanger would rapidly lose its ability to cycle. The performance degradation resulted from massive disproportionation. A major focus of development was the engineering of a new alloy capable of withstanding high temperatures, as well as meeting the other performance requirements of the system.

Ergenics has extended its original disproportionation-proof alloy development to the search for compressor alloys that can survive elevated temperatures.

High Temperature Soak Tests

During its original high temperature alloy development work in the mid 1990's, Ergenics developed a "Soak Test" procedure to screen alloy candidates (see Table 1). An alloy sample is placed within a test reactor vessel and is fully hydrided at high pressure. The test vessel is then held at high temperature for an extended duration to try to induce disproportionation. Pressure is monitored during the test. The temperature is high enough that a small amount of hydrogen is lost via diffusion through the reactor vessel wall. This diffusion loss is manifested by a small pressure decrease during the test. A pressure decrease in excess of the amount anticipated for diffusion may indicate alloy disproportionation.

Table 1 - Ergenics' Soak Test Screens Alloys for High Temperature Applications

Soak Test Procedure:

1. Fill alloy with hydrogen in test vessel at room T and high P
2. Reduce P, but stay above plateau P
3. Weigh vessel
4. Heat vessel, hold high T and monitor P loss
5. After time, isolate vessel and weigh to determine H_2 content (loss)
6. Replace lost H_2
7. Reheat vessel to see if P returns to original high level

The test reactor is subsequently weighed to rule out whether pressure loss not due to diffusion might be attributed to leakage. Finally, the sample is refilled with hydrogen to ascertain cycle-ability.

Figures 2 and 3 show the soak test results for two alloy candidates, one that experienced performance loss (Figure 2) and one that did not (Figure 3).

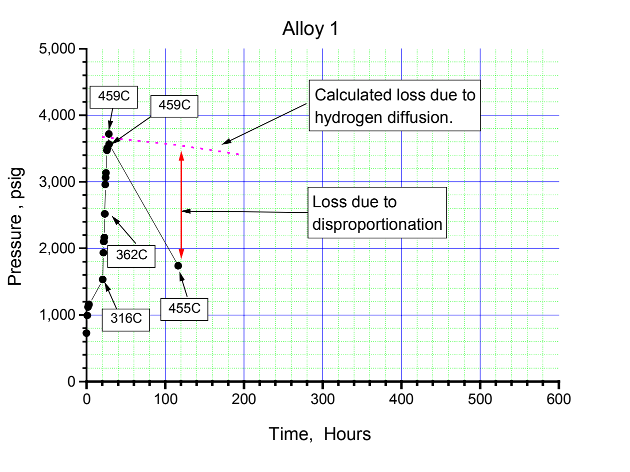

Figure 2 - Soak Test results showing disproportionation.

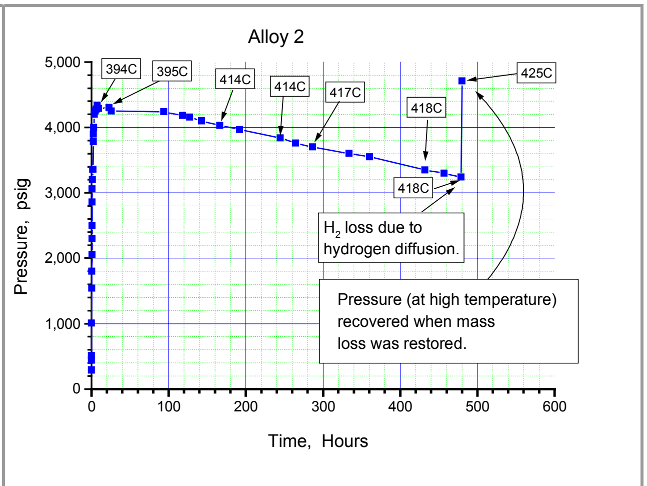

Figure 3 - Soak Test results for an alloy that is stable at elevated temperature.

Conclusions

Increasing the heating fluid temperature of a hydride “thermal” hydrogen compressor from 80°C to 130°C more than doubles efficiency while reducing system complexity, size and cost. If natural gas is available as the heating source, energy costs can be three times lower than for an electric-motor-driven mechanical compressor.

Disproportionation proof alloys that will survive elevated temperature operation have been engineered.

Future Work

The entire thermal compression process will be validated in a pilot scale system that includes both the single stage (first stage) used for purification studies and subsequent stages needed to boost hydrogen pressure to over 5,000 psig. The flow rate capability of the pilot-scale system will be similar to that required for overnight refueling of a hydrogen fuel cell automobile.

Acknowledgement

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References

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