Metal-hydride hydrogen compressors for laboratory use

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Keywords: metal hydride, hydrogen, compressor

Abstract
The development of commercial applications of hydrogen at high pressure (300–700 bar), for example in fuel cell vehicles and associated filling stations, necessitates the study of hydrogen capacity, and the safety of materials at pressures well above that of standard pressurised cylinders employed in research laboratories. This, in turn, requires laboratory instruments to have some mechanism for hydrogen compression as part of their operation. In this study, the use of metal-hydride compressors for laboratory applications is explored and evaluated. The reduced operating requirements of laboratory instruments, relative to industrial compressors, and the ready availability of laboratory heating and cooling methods, allows the use of relatively simple, single-stage metal-hydride compressors. A simple theoretical derivation enables the determination of the size and amount of hydrogen storage alloy required for a desired pressure, given the experimental volume to be pressurised. Practical requirements, both in terms of the hydrogen storage alloy, and of the pressure vessel, are discussed. Examples of working compressors for both manual operation to 1000 bar, and automated operation to 100 bar, under computer control, are also given.

1. Introduction
Hydrogen storage materials able to store and release hydrogen at pressures of hundreds of bar are increasingly of interest. One driver of this interest is the possibility of enhanced high-pressure hydrogen storage for fuel-cell vehicles, which operate with hydrogen tank pressures of 350–700 bar. Another important application of high-pressure hydrogen is in studies of embrittlement in structural materials for the hydrogen economy, such as pipeline steels. Since laboratory gas cylinders typically contain hydrogen at less than 200 bar when full, compression is necessary to study materials at higher pressures. The small amount of hydrogen generally used in laboratory studies means that motorised mechanical compressors are not well suited to this application.

The same interstitial metal hydrides (MH) used to store hydrogen at a roughly constant temperature are also able to absorb hydrogen at a low pressure and to desorb it at much higher pressure when heated, thus forming a simple one-shot compressor. Reversing the sequence means that hydrogen can be reclaimed rather than exhausted from the system, which is highly advantageous when using the much more expensive deuterium isotope, as well as making safety requirements easier to meet. Additionally, the same gas, ideally without loss, may be used many times, so that new impurities are not introduced into the apparatus by constantly recharging it from a gas cylinder. Lastly, nearly all the gas in a gas cylinder can be used, since the supply (suction) pressure of the compressor can be much lower than the maximum cylinder pressure. The review by Lototskyy et al [1] compares MH materials for compressor service, and provides a valuable resource for the selection of materials.

In the present context, a simple MH compressor for laboratory use, operating at up to 340 bar, may be easily constructed by loading a suitable hydrogen-storage alloy into a commercial sample cylinder.¹

¹The pressure rating at the maximum operating temperature, the compatibility of the cylinder material with hydrogen and the packing fraction of the metal hydride must be taken into account to ensure safe operation.
Combining a custom-designed pressure vessel with a suitable hydrogen storage alloy can readily extend the available pressure range to over 1000 bar, and choosing a suitable material with high thermal conductivity would speed up the heating and cooling processes. Simply heating a cylinder of LaNi5 with a hand-held hot-air gun can generate 100 bar within a few minutes. Furthermore, adding computer-controlled heating and cooling allows the compressor to be automated as part of the operating procedure of a Sieverts apparatus or microbalance for measuring hydrogen uptake, and the compressor may be configured as a programmable variable pressure source.

In this paper, the principles and practice of using MH compressors in the laboratory are discussed.

2. Metal-hydride compressor principles

Metal hydrides employed in hydrogen storage are usually interstitial alloys of hydrogen with a metallic alloy or an intermetallic compound, rather than covalent (e.g. alanates) or ionic (e.g.) NaH, and interstitial hydrides are the materials best suited to compressor service. Equilibrium between the surrounding hydrogen atmosphere and the absorbed hydrogen species (‘atoms’) is described to a good approximation by the van ‘t Hoff relation in the form

\[ R T \ln \left( \frac{p_{\text{abs}}}{p_0} \right) = \Delta H - T \Delta S \]  

(1)

for the reaction in which a dilute solid-solution phase (α) transforms to a concentrated hydride phase (β). Here, \( \Delta H \) and \( \Delta S \) respectively denote the enthalpy and entropy change per mole of \( H_2 \), corresponding to the formation of the MH, referred to pressure \( p_0 \). Equation (1) presumes that absorption takes place at a constant pressure \( p_{\text{abs}} \), observed as a plateau in the pressure–composition isotherm. An equivalent expression can be written for desorption at notionally constant lower pressure \( p_{\text{des}} \), implying pressure hysteresis, with slightly different values of \( \Delta H \) and \( \Delta S \). Figure 1 shows the van ‘t Hoff lines for a selection of metal–H\(_2\) systems. The slope of the van ‘t Hoff line corresponds to \( \Delta H/R \), and the intercept at \( T \to \infty \) to \( \Delta S/R \), both per mol. H\(_2\). Metal–metal-hydride equilibrium lines with a high slope (e.g. Mg–H\(_2\)) correspond to relatively stable hydrides, while those with a low slope (e.g. TiCrMn–H\(_2\); #31 in figure 1) are relatively unstable. Real MH isotherms exhibit plateau slope, and the measurements of \( p_{\text{abs}} \) and \( p_{\text{des}} \) are made at the centre of the relevant plateau.

The strict relationship between plateau pressure and temperature in equation (1) implies that metal hydrides can be used to make a compressor with no moving parts other than as necessary for heat management.

The description based on equation (1) is highly idealised, but serves to elucidate how the thermodynamic characteristics of particular metal hydrides, summarised by \( \Delta H \) and \( \Delta S \), establish the possibilities for designing a metal-hydride compressor based on those hydrides. Conversely, establishing a design performance, typically summarised by the achievable compression ratio between maximum and minimum working temperatures, constrains the thermodynamic parameters of the metal hydride to be used. To build a high-performance compressor, the plateau slope, pressure hysteresis, and kinetics, which is dominated by the effective thermal conductivity of the hydride bed, must be taken into account, although this level of care is unlikely to be required for a laboratory compressor.

Figure 2 shows the concept of a single-stage MH compressor working between pressures \( p_l \) and \( p_h \), based on heating to a temperature \( T_h \) to desorb hydrogen, and cooling to a temperature \( T_l \) to initially charge the compressor, or to re-absorb hydrogen.

For a single MH stage working between temperatures \( T_l \) and \( T_h \), and assuming that \( \Delta H \) and \( \Delta S \) are independent of temperature and equal for absorption and desorption, equation (1) yields

\[
\ln \left( \frac{p_h}{p_0} \right) = \frac{1}{R} \left( \Delta S - \frac{1}{T_l} \Delta H \right)
\]

\[
\ln \left( \frac{p_l}{p_0} \right) = \frac{1}{R} \left( \Delta S - \frac{1}{T_h} \Delta H \right)
\]

Defining the compression ratio as \( \rho = p_h/p_l \),

\[
\ln \rho = \frac{1}{R} \left( \frac{1}{T_l} - \frac{1}{T_h} \right) \Delta H.
\]

(2)

Equation (2) shows that the compression ratio depends on the MH material through \( \Delta H \). For a single stage, high \( \Delta H \) gives the highest compression ratio between a given pair of working temperatures, and (the assumed constant) \( \Delta S \) has no influence in this ideal case. On the other hand, the primary design goal is
Figure 1. Van ‘t Hoff plots for selected metal–H₂ systems, based on [1] (numbered lines) with classic absorbers Mg and LaNi₄Al added for reference. The numbers correspond to [1] table 1, which lists the sources of the plotted data. 1: V₇₅Ti₁₇.₅Zr₇.₅. 4: V₉₅Ti₁₀Zr₇.₅Cr₇.₅. 5: LaNi₄₄Sn₈₂. 8: LaNi₅. 10: V₀.₉₅Ti₀.₁₀Fe₀.₀₅. 11: TiFe₀.₁₀Mn₀.₁₀. 18: MnNi₄₅Fe₀₅. 25: TiCr₁.₉Mo₀.₁₀. 31: TiCrMn. 32: ZrFe₁.₈Ni₀.₂. 33: Ti₀.₈₆Mo₀.₁₄Cr₁.₉. Red: AB⁵. Blue: AB⁴. Green: AB. Black: BCC V-based solid-solution. Solid lines: reported measurement range. Dashed lines: extrapolation within [0.1, 1000] bar and (–50, 200) °C. Dashed box: hypothetical operating area for a 350-bar compressor. The linear relationship between log(pₓₑₛ) and 1/T confirms that equation (1) is obeyed.

Figure 2. Metal-hydride compressor concept based on a van ‘t Hoff plot. Hydrogen is absorbed at pₛ, while heat Qₑₓᵣᵣ is rejected at Tₛ. Heating to Tₕ desorbs hydrogen to the receiving vessel at pₓₑₛ while heat Qₑₓᵣᵣ is absorbed.

probably a set value of delivery pressure, rather than compression ratio. Since high pₓₑₛ implies low ΔH for a given Tₕ (figure 1), selecting a material to achieve the desired pₓₑₛ within an acceptable range of working temperatures becomes a complex task of optimisation with conflicting constraints. An advantage of working under laboratory conditions to compress small amounts of hydrogen with modest throughput is that a wider
range of temperatures is usually available than in the case of an industrial compressor, which typically must use solar power or process waste heat to reach $T_h$, and a heat exchanger exhausting to ambient for $T_l$.

3. Laboratory implementation of a metal-hydride compressor

3.1. Experimental requirements
Here, the most important requirements are the maximum pressure to be generated ($p_h$), the minimum pressure at which hydrogen is to be reabsorbed ($p_l$), and the temperatures ($T_h$, $T_l$) at which these pressures are reached in thermal equilibrium. The operating area for a hypothetical system for which $p_l = 1$ bar, $p_h = 350$ bar, $T_l = -20$ °C, and $T_h = 200$ °C is indicated in figure 1. Setting the operating area immediately restricts the choice of feasible metal hydrides. In the case illustrated, \( V_{0.85 Ti_{0.10} Fe_{0.05}} \) is a viable choice, with some other alloys potentially viable if the temperature limits are relaxed. It should be noted, however, that published van’t Hoff lines are typically drawn for desorption; hysteresis has not been taken into account.

A low value of $p_l$ is desirable, particularly when using D$_2$, but the correspondingly low value of $T_l$ could be impractical in terms of available equipment, such as a circulating coolant bath. Furthermore, the kinetics of absorption slows rapidly as $T_l$ is reduced, and may cause reabsorption to stagnate at a pressure above the equilibrium corresponding to $T_l$. Nevertheless, in the authors’ experience, judicious use of liquid nitrogen (77 K) can achieve values of $p_l$ much lower than 1 bar; although reabsorption by the MH may have stagnated, the free gas in the void volume of the compressor continues to condense. The temperature ratings of the cooled components must be taken into account.

Presuming that the MH material is suitable, the feasible upper limit to $T_h$ is set relative to the lowest temperature rating among the materials that are heated to $T_h$. This aspect is considered in §3.4.3.

3.2. Choice of MH material
Having identified candidate MH systems compatible with the ranges ($p_l$, $p_h$) and ($T_l$, $T_h$), several other factors should be considered in settling on a final choice of MH material. Full (absorption and desorption) pressure–composition isotherms need to be measured at $T_l$ and $T_h$ to determine the correct values of $p_l$ and $p_h$, due to the effects of pressure hysteresis and plateau slope.

3.2.1. Activation
Activation is the process of forcing the first formation of the hydride in the virgin hydrogen storage alloy. The requirements are highly variable between alloy systems, but the required conditions must be achievable within the design limits of the compressor vessel and its peripheral components, unless the activation is carried out externally. In the case of some AB$_2$ alloys, temperatures as high as 400 °C may be required to breach the surface oxide layer, so the compressor vessel and seals (see §3.4.3) must be compatible. AB$_3$ alloys tend to be less demanding in this respect, with exposure to hydrogen at temperatures below 100 °C typically sufficient. If the MH cannot be activated in situ, then transfer under an inert atmosphere will be required, as small amounts of hydrogen can remain trapped in the material following evacuation, and in many materials decrystallisation during hydriding reduces the particle size (<300 nm in some materials), making the material highly flammable on exposure to air.

3.2.2. Pressure hysteresis
figure 2 illustrates the effect of pressure hysteresis on the van’t Hoff plot, based on pressures notionally measured at the centres of the absorption and desorption plateaux. At $T_h$ the MH is in desorption, whereas at $T_l$ it is in absorption. The greater the hysteresis, typically measured as $p_{abs}/p_{des}$, the smaller the achievable compression ratio becomes, as compared to a material with no hysteresis.

3.2.3. Plateau slope
A real MH system absorbs in a range of pressures, likewise for desorption. Therefore the minimum $p_h$ occurs at the low-concentration end of the two-phase desorption isotherm at $T_h$, while the maximum $p_l$ occurs at the high-concentration end of the two-phase absorption isotherm at $T_l$. Plateau slope also decreases the achievable compression ratio. The combined effects of pressure hysteresis and plateau slope are illustrated in figure 3, based on isotherms for LaNi$_5$ measured by the authors. The upper temperature of the MH ($T_h = 80$ °C) is achievable with waste heat, and the lower temperature ($T_l = 40$ °C) is achievable with air cooling, but the compression ratio is only about 2, compared to about 6 for a case with no plateau slope and hysteresis.

3.2.4. Kinetics
Unless a very effective heat exchanger is embedded in the MH, the absorption and desorption kinetics are dominated by heat flow, as was demonstrated by Goodell and Rudman many years ago [2]. The problem is
the powder morphology of most metal hydrides. For example, while the thermal conductivity of a solid composite compact of LaNi$_5$ powder is greater than 30 Wm$^{-1}$ K$^{-1}$ [3], the effective thermal conductivity of a LaNi$_5$ powder bed (with porosity ~0.5) is only around 1.3 m$^{-1}$ K$^{-1}$ [4]. If the compressor is required to respond quickly, e.g. with a time constant of seconds, then great care with the internal construction (MH form and arrangement, heat management) becomes necessary. Combining and compacting the MH material with a thermal conductor such as aluminium [5] or graphite [6] can significantly enhance the effective thermal conductivity. For a high-pressure compressor, the wall thickness of the containment increases compared to the thickness of the contained MH bed, so that the thermal conductivity of the pressure vessel itself may influence the overall kinetics. Given that for most laboratory experiments, such as isotherm measurements, the compressor is quite small, and rapid changes of pressure are not essential, a simple but slow MH compressor is likely to suffice in most cases.

3.2.5. Factors affecting lifetime

Particularly when connected to an automated system in which the pressure is changed frequently, the lifetime of the MH is an important consideration. The following examples of reduction of lifetime relate to LaNi$_5$, about which far more is known compared with other candidates for laboratory compressor service. The amount of hydrogen able to be stored and desorbed tends to decrease with absorption–desorption cycling. One cause is the thermodynamic metastability of the hydride phase, as is the case for $\beta$-LaNi$_5$, which disproportionates to LaH$_3$ + Ni if held in the $\beta$ phase at much above 100 °C [7]. A likely related cause in the case of LaNi$_5$ is the incremental sequestering of hydrogen (‘trapped hydrogen’) which is observed in successive cycles at elevated temperature when the absolute amount of hydrogen in the system is tracked [8]. Another cause is the reaction with impurities in the hydrogen gas, forming O-containing phases that do not absorb hydrogen, observed as an incremental increase in the mass of a hydrided sample during successive cycles carried out in a gravimetric hydrogenator. Interestingly, it has been reported [9] that 1000 cycles of closely stoichiometric LaNi$_5$ in extremely pure hydrogen at room temperature led to no observable degradation. Amorphisation of the material with cycling can also reduce hydrogen capacity, leading to further degradation.

The question of possible in-situ regeneration of the MH is significant in the case of a large, high-value compressor. Very little is known about this aspect in relation to most candidate MH materials. In the case of LaNi$_5$, the authors have observed (by in-situ neutron diffraction) that any disproportionation is reversible by heating under vacuum at 200 °C. Reactivation following accidental exposure to air or the accretion of impurities from the hydrogen supply may also be possible. Once again, the authors have found this to be the
case for LaNi₅. In the case of amorphisation, the MH would require annealing to restore its crystallinity, and this would require an ex-situ heating process, as the temperatures are likely to be too high for a compressor container.

### 3.3. Compressor volume and amount of hydride

In a typical experiment, the compressor is required to charge a volume (the experimental volume, \( V_{\text{expt}} \)) at temperature \( T_{\text{expt}} \) with hydrogen to pressure \( p_h \). Whether this happens in a single compression or in a stepped sequence does not alter the total amount of gas, \( n_{\text{expt}} \), to be supplied. In addition, the compressor must charge its own void volume (\( V_{\text{void}} \)) to the same pressure. Ignoring any connecting pipework in the interest of simplicity, when the MH is fully discharged to \( \alpha \) phase at temperature \( T_h \), the total amount of gas desorbed is thus

\[
n_{\text{gas}} = n_{\text{expt}} + n_{\text{void}}
\]

and the MH must be able to store and release at least this much hydrogen. If the reversible storage capacity of the MH is \( w \), expressed as the weight fraction of hydrogen to the sample plus hydrogen, the mass of \( \alpha \) phase (essentially the mass of hydrogen storage alloy) required to release \( n_{\text{gas}} \) moles of H₂ is

\[
m_\alpha = \left( \frac{1 - w}{w} \right) M_H n_{\text{gas}}.
\]

To allow for expansion when hydrogen is (re)absorbed, the empty volume of the compressor vessel, \( V_{\text{comp}} \) must be filled to a fraction \( \Phi < 1 \). The expansion of the MH will vary for different materials, in terms of the unit cell crystal expansion and the packing of the powder grains, which typically decrease significantly in size during the first few cycles. For LaNi₅, which expands by 24% to form the \( \beta \) phase, the maximum permissible value is thus \( \Phi \approx 0.8 \) to avoid compressing the MH and causing mechanical stress to the vessel. If the packing factor for the MH material is \( \phi \), with a typical value around 0.5 for loose metal powder, then the volume occupied by the desorbed MH is

\[
V_\alpha = \frac{m_\alpha}{\rho_\alpha} = \Phi \phi V_{\text{comp}}
\]

where \( \rho_\alpha \) is the density of the \( \alpha \) phase (or alloy, approximately), and the void volume is

\[
V_{\text{void}} = (1 - \Phi \phi) V_{\text{comp}}.
\]

Rewriting equation (3) as \( V_{\text{comp}} = \frac{n_{\text{expt}}}{n_{\text{gas}} / V_{\text{comp}} - n_{\text{void}} / V_{\text{comp}}} \), and using equations (4)–(6) gives the following for the required internal volume of the compressor:

\[
V_{\text{comp}} = \frac{\frac{p_h V_{\text{expt}}}{Z(p_h, T_{\text{expt}})RT_{\text{expt}}} - \frac{1}{1 - w} - (1 - \Phi \phi) \frac{p_h}{Z(p_h, T_h)RT_h}}{\Phi \phi \frac{p_h}{Z(p_h, T_h)RT_h}}
\]

where \( Z \) is the compressibility of H₂. The first term in the denominator of equation (7) concerns the total amount of hydrogen to be stored and released by the MH. The second denominator term concerns the amount of gas required to charge the compressor void volume to \( p_h \). The numerator represents the amount of gas in the instrument required for the experiment, and clearly this depends on the temperature of the system. Experiments at low temperatures, such as 77 K, will require a larger compressor volume to supply sufficient hydrogen. Where the instrument has two temperature zones, such as a reference volume at or near ambient temperature, and a sample cell at 77 K, the numerator can be readily replaced by the appropriate sum over the different temperature volumes, such as \( \frac{p_h V_{\text{expt}}}{Z(p_h, T_{\text{expt}})RT_{\text{expt}}} + \frac{p_h V_{\text{expt}}}{Z(p_h, T_h)RT_h} \). The equations above may then be used to calculate the required mass of \( \alpha \) phase (alloy) etc.

### 3.4. Containment

#### 3.4.1. Pressure vessel

For a thick-walled pressure vessel with inner radius \( r \), the required wall thickness \( t \) for given design pressure \( p \) and design tensile stress \( \sigma \) of the material at the working temperature is obtained using

\[
K^2 = \frac{\sigma + p}{\sigma - p}
\]
where $K$ is the ratio of the outer to the inner cell radius, and $t = r(K - 1)$. The value of $\sigma$ is set by national standards for common materials, or by applying a safety factor to the yield strength or ultimate tensile strength of less-common materials. Typically, $p$ is defined as 1.1 times the rated working pressure at the working temperature.

As $p$ increases towards $\sigma$, equation (8) shows that $K$ increases rapidly, so that a high-pressure vessel may become very heavy. At high pressure, a practicable vessel is likely to be a long, slender cylinder for this reason, so the vessel mass may be estimated by ignoring the ends, yielding for the mass:

$$m \approx \rho V_{\text{comp}} \left[ (1 + K)^2 - 1 \right]$$  \hfill (9)

where $\rho$ is the density of the cylinder material. If vessel mass is a factor in the use of the compressor, high-strength materials should therefore be considered in order to reduce the value of $K$ in equation (8).

Equations (7)–(9) form the basis for designing the compressor cylinder.

### 3.4.2. Material compatibility with hydrogen

Common austenitic stainless steels, particularly AISI 316, are suitable for hydrogen service at pressures up to hundreds of bar, owing to their resistance to hydrogen embrittlement [10], and also exhibit modest temperature derating factors. The stronger precipitation-hardenable stainless steels are well known to suffer hydrogen embrittlement, and should not be used. Special variants, such as 316(Ti) are used for commercial valves and fittings for use to several kbar hydrogen pressure, but these alloys are not readily available.

High-strength aluminium alloys (e.g. 7075) are well known to be highly resistant to hydrogen, but are only suitable for modestly elevated temperatures, in most cases well below 200 °C.

Titanium-based alloys are generally susceptible to hydrogen embrittlement, and should not be used. The approach of plating the interior of such a vessel with Au or Ag to protect it is dangerous, in the authors’ view, since pressure from any sharp metal particles so contained may breach the coating.

High-strength Fe- and Ni-based alloys, e.g. Inconel 718, are commonly used by industry at high temperatures, due to their high resistance to corrosion. However, Inconels are also subject to hydrogen embrittlement to some degree, below about 200 °C [11].

The high-strength high-temperature alloy AISI 660 (Superalloy A286), while less strong than the Inconels, is reported to be highly resistant to hydrogen embrittlement [12].

High-strength Cu(Be) alloys are used commercially to manufacture components for very high-pressure hydrogen service, but the maximum temperature for these is limited to below about 275 °C, so as to avoid over-aging or annealing [13]. Cu(Be) alloys also have high thermal conductivity compared to stainless steels, which may improve the response time of the compressor if the vessel walls are very thick and the MH bed is slender. These alloys require special precautions during machining, owing to the toxicity of beryllium oxide. In service, the exterior surfaces should be protected from corrosion for the same reason. The authors find that nickel plating is satisfactory.

While design tensile strengths are typically set for common materials in national standards, values for some of the materials mentioned above may need to be assigned in consideration of the mechanical properties of the alloy, for instance via a safety factor relative to yield strength or ultimate tensile strength.

### 3.4.3. Seals and connections

Loading the compressor with metal, sealing the vessel, and preventing the hydrogen-cycled metal or hydride escaping during desorption are vitally important practical matters to be dealt with when designing the compressor vessel. The temperature rating of the compressor is that of its lowest-rated component. If the containment is fully welded, the temperature rating is essentially that of the vessel itself. However, it is easier to load the compressor if a port into which a funnel can be inserted is available. Again, for a simple compressor, a commercial austenitic stainless-steel sample cylinder rated at 344 bar, with a threaded port which can be sealed after loading using Teflon tape is convenient, and is appropriate for pressures of up to about 300 bar, with appropriately rated fittings at a temperature of 200 °C. Other connection types, such as metal-to-metal fittings, are also possible, although these may be more expensive, provided the specifications meet the required temperature and pressure requirements, and the opening is of sufficient size to enable loading. A threaded port also gives flexibility as to the technology selected for fittings, pipework, and valves.

For a custom-built compressor, higher pressures using appropriate containment materials are possible, with 1000 bar readily achievable. A threaded port of sufficient internal diameter also simplifies machining access. If the heated components include elastomeric O-rings, then these are most likely to have the lowest temperature rating, e.g. about 100/150/200 °C for Neoprene/Viton/silicone.

A further point to note is that at $T_h$, the vessel itself must be de-rated with respect to its pressure rating at room temperature. For 316 stainless steel, a 90% derating at 200 °C is common.
A filter preventing the escape of metal or hydride from the compressor is essential for at least two reasons: (i) the dehydrided MH is typically formed by fracturing larger metal particles during activation (the first absorption of hydrogen), and the resulting sharp particles damage valve seats, preventing tight shutoff, and (ii) escaped MH constitutes an unaccounted-for sink/source of hydrogen within the attached system, which in the case of a Sieverts hydrogenator may have a deleterious effect on the accuracy of measurements of hydrogen uptake by the sample being studied. Filters with micron pore sizes are ineffective in this role, as the size of MH particles can be less than 300 nm. Although expensive, commercially available filters with nm pore sizes are effective in the authors’ experience, but have limited pressure ratings. For pressures above about 200 bar, the authors embed a chromatography frit in a threaded fitting, held in place by a hollow socket-headed screw in a thread tapped along the fitting axis.

3.4.4. Leak integrity
Given that the MH is likely to be finely divided and highly flammable after hydrogen cycling, it is important to make the compressor leak-tight, not only to prevent the escape of a flammable gas, but to avoid the consequent disassembly required to re-make the leaking seal, which needs to be performed under an inert atmosphere. From this point of view, all-metal and Teflon seals are a better choice than elastomeric O-rings, which have a finite lifetime in service. Leak checks are best performed at the maximum and minimum temperatures to be used.

3.4.5. Mechanical forces owing to MH expansion
Classic hydrogen storage alloys typically expand during the α–β transformation, and may cause very high tensile stress in the vessel walls if insufficient void volume is available to accommodate the expansion. In §3.3 the total occupancy of $V_{\text{comp}}$ was split into a factor $\Phi$ accounting for the porosity of the hydride, whether a powder or a compact, and the fraction $\Phi$ of $V_{\text{comp}}$ occupied by the porous MH. Setting $\Phi$ to be the reciprocal of the relative volume expansion from bare metal to fully charged MH at least in principle accommodates the expansion, without compression of the porous MH bed itself, i.e. without an increase in $[\phi]$. In reality, friction with the vessel walls may prevent the MH bed from expanding isotropically. In the typical case of a vertical cylinder, the MH expansion along the cylinder axis may be restricted by friction, causing dangerous radial forces on the wall. This topic is briefly reviewed by Hu et al [14]. In the authors’ view the friction effect is likely to be ameliorated in tall and slender vessels by the lower cylinder end being internally hemispherical or conical, and thus forcing some displacement of the expanding MH powder along the cylinder axis. Another approach is to mount the cylinder horizontally, so that the free surface area of the MH mass is large, and the curved walls encourage vertical displacement of the powder as it absorbs hydrogen.

3.5. Automation
Automation requires a means of heating and cooling the compressor under external control. This can be as simple as immersing the compressor in a fluid bath able to operate between $T_l$ and $T_h$ under computer control. The simplest scheme is to emulate a gas cylinder by maintaining the compressor at a sufficiently high value of $T_h$ to supply hydrogen at the maximum required experiment pressure, and to emulate an exhaust to ambient or vacuum pump by maintaining the compressor at $T_l$. Depending on the type of experiment to be supplied, stepping the pressure up and down by controlling the compressor temperature between $T_l$ and $T_h$ may be desirable, for instance to minimise the time spent at temperatures where the MH might disproportionate.

For $T_h > 100 \degree C$ a ‘dry’ means of heating is desirable to avoid handling expensive thermal oils at hazardous temperatures. A scheme that is relatively simple to implement is to use a temperature-controlled cartridge heater attached to or embedded in the compressor vessel, in combination with a refrigerated bath circulating through a heat exchanger also attached to or embedded in the compressor. At pressures below that corresponding to ambient temperature in the compressor, the refrigerated bath controls the compressor, while at higher pressures the electric heater controls it. If the refrigerated bath is also able to be heated, an overlap in temperature with the electrical heating will smooth the transition between cooling and heating regimes.

A simple implementation of this scheme is to machine a close-fitting thermally conducting shroud to carry the heater and cooling heat exchanger, and clamp or slide it onto a cylindrical compressor vessel, with thermally conducting paste in-between. For a faster response, heating and cooling can be built into the compressor itself, although it thereby becomes far more complicated.

However the thermal management is implemented, thermal insulation is necessary, both for safety and to achieve reasonably uniform heating/cooling of the compressor.
Figure 4. Manually operated MH compressor delivering 1000 bar using a hot air gun [15]. For absorption, the compressor is cooled with liquid nitrogen, typically achieving pressures below 1 bar. R: the MH reservoir, serving as a compressor when heated. \( V_{\text{ref}} \): hydrogenator reference volume. P: pressure transducer.

3.6. Examples

3.6.1. Simple manual compressor for 1000 bar

As an example of a simple high pressure laboratory compressor, the dimensions and amount of alloy for a compressor required to charge a 10 cm\(^3\) experiment volume (e.g. a Sieverts hydrogenator) to 1000 bar at ambient temperature by heating the compressor to 473 K are now calculated. A filling factor of \( \Phi = 0.72 \) with a packing fraction of \( \phi = 0.5 \) was chosen, as this corresponds to a useful rule of thumb of \( \sim 3\ \text{g cm}^{-3} \) AB\(_5\)-type MH alloy. The required compressor volume is \( V_{\text{comp}} = 31.2\ \text{cm}^3 \), containing approx. 95 g of alloy.

Having determined \( V_{\text{comp}} \), a practical design is founded on a combination of material and dimensions. It should be borne in mind that the detailed design of a pressure vessel should be done by a suitably qualified person, in line with local regulations; the following is an example of the process only.

Of the commonly available austenitic stainless steels, 304 grade is unsuitable, and 316 grade is only marginally suitable for high-pressure service [10]. Moreover, the design tensile strength of some tempers of 316 stainless steel at 200 °C is lower than the present design pressure (110 MPa), so a stronger alloy should be used, since the denominator in equation (8) must be positive. Even if a stronger temper of 316 grade were available, so that e.g. \( \sigma = 130\ \text{MPa} \) at 200 °C, the cylinder walls would need to be very thick (\( K = 2.46 \) from equation (8)), very heavy (\( m = 4.7\ \text{kg} \) from equation (9) ignoring the ends), and have a very high thermal mass compared to that of the contained MH. AISI 660 grade is far stronger, and is reported to be safe with hydrogen [12], but is very expensive and not readily available in small quantities.

A cheaper and even stronger alternative is Cu(Be), subject to the aforementioned toxicity concerns. A readily available alloy is UNS C17200, ASTM temper TD04 (cold-worked, hard), with a yield strength of 620–790 MPa at room temperature, according to manufacturers’ data. Ageing for 2 h at 316 °C produces the ASTM TH04 temper, with yield strength 1140–1410 MPa at room temperature, according to manufacturers’ data. A Material Certificate stating the mechanical properties of the actual manufacturing batch from which the employed alloy is taken should be obtained as a basis for the design process. For the purpose of this
example, alloy C17200 with TH04 temper and an average yield strength of 1275 MPa at room temperature, is assumed.

A convenient internal diameter is 17.87 mm, which is the tapping-drill size for a 1/2-inch NPT thread, to be sealed with Teflon tape, and also to be compatible with many high-pressure fitting technologies that could potentially be used to construct the attached gas manifold. A length of 125 mm then provides the required $V_{\text{comp}}$. Three further factors must be taken into account. Firstly, the maximum service temperature of 200 $^\circ$C requires the application of a strength derating factor of about 90%, according to manufacturers’ data. Secondly, a value for the design tensile strength needs to be established. Here, it will be assumed to be 60% of the derated yield stress, i.e. 689 MPa at 200 $^\circ$C. Thirdly, the threaded open end of the cylinder (the female connecting port) needs thickened walls because (i) the major thread diameter (21.34 mm in this instance) is in principle exposed to the pressurised hydrogen and (ii) inserting the mating tapered threaded fitting will cause extra hoop stress. If a simple cylindrical profile is maintained, rather than thinning the cylinder body relative to the threaded port, then the body will be ‘over-engineered’, but very conservatively rated. Using equation (8) gives $K = 1.175$, and an outer diameter of 21.0 mm for the cylinder body. The required body wall thickness is consequently only 1.56 mm, which is impractically thin relative to the likely accuracy of the internal machining over the length of the compressor, unless special care is taken. For the port, the

Figure 5. Working 100 bar hydrogen and deuterium MH compressors. The heat of absorption is removed using a temperature-controlled water/glycol bath, and heat is supplied for desorption with cartridge (rod) heaters powered by PID controllers. R: thermally insulated MH reservoir ($\text{LaNi}_5$) based on a 500 cm$^3$ commercial 316-grade stainless-steel sample cylinder. F: secondary commercial 500 nm filter. T: temperature control thermocouple (the rod heaters are embedded and not visible). W: cooling water circuit. S: solenoid valve to admit coolant.
corresponding outer diameter is 25.08 mm, before an allowance for inserting the mating fitting is made. Machining the compressor from a readily available bar of 1 inch (25.40 mm) diameter is thus convenient.

Figure 4 shows a MH compressor fabricated from CuBe (nickel-plated), similar to but longer than the example above, equipped with a 1/2 inch NPT adapter, a 4 kbar stainless steel pipe, and a 1 kbar isolation valve connecting it to a 1 kbar manifold. The cylinder body is not thinned relative to the connecting port. A 50 nm filter frit is embedded in the adapter.

To generate a pressure of hydrogen, the isolating valve is slowly opened to the desired instrument volume, and the compressor is heated with a hot air gun. In the authors’ experience, heating for 10–15 min. suffices to reach 1000 bar, the rate-limiting factor being in this case the effective thermal conductivity of the MH bed, owing to the low thermal mass and high thermal conductivity of the compressor cylinder. Removing the heat source halts the pressure increase within a few seconds, so provided that the operation is continuously attended, overshooting the desired or safe pressure is not likely. When the desired pressure is reached, the isolating valve is closed and the heat source removed, although it should be borne in mind that the poor thermal conductivity of a MH bed means that stored heat will increase the pressure within the compressor after the valve is closed. Significant adiabatic heating of the experiment volume is likely. With experience, a small overshoot may be judged so that the desired pressure is reached after the temperature settles.

To absorb hydrogen back into the compressor, the isolating valve is slowly opened, and the compressor is immersed in a dewar containing coolant, which may be liquid nitrogen. Applying liquid nitrogen first at the bottom of the compressor only, then progressively higher as the MH absorbs, reduces the likelihood of kinetically stalling the absorption process.

### 3.6.2. Fully automated compressor for 100 bar

Figure 5 shows a dual automated reservoir for supplying H₂ and D₂ to a gravimetric hydrogenator based on a microbalance. The gas manifold is also equipped with a reference volume, so the total experimental volume is approximately 800 cm³. Accordingly, the reservoirs are based around a commercial 500 cm³ 316 grade sample cylinder, rated at 124 bar at room temperature, sealed with Teflon tape, fitted with an aluminium shroud carrying a 300 mm, 500 W rod heater, a coaxial coolant injector, and a thermocouple, wrapped in thermal insulation, and held in a stainless-steel jacket. Each cylinder is loaded with 1.5 kg of LaNi₅. The heaters are managed via PID temperature controllers under the command of a control computer. A lookup table relates the previously measured equilibrium pressure to the compressor temperature in both absorption and desorption, with fine adjustment via a software feedback loop that reads the pressure in the compressor. A refrigerated circulator with 600 W cooling power, filled with a water/ethylene-glycol mixture, provides cooling to about −10 °C for re-absorption to less than 1 bar. The coolant temperature and solenoid valves are also under computer control.

This arrangement gives great flexibility in the use of the attached hydrogenator. In isotherm mode, a specific pressure in the reference volume is requested from the reservoir in use, and admitted to the microbalance through a needle valve. The pressure over the sample is thus stepped up in the desired
sequence. This is a much gentler and more consistent process than opening the manifold to the maximum experimental pressure, set on a gas cylinder regulator.

Figure 6 shows pressure rise as a function of time for this compressor, with a desired final pressure of 100 bar. The volume to be charged by the compressor was 158 cm$^3$, and this was achieved over 60 min, with an accuracy of 0.01 bar, and a maximum overshoot of 1.7 bar.

4. Summary

Based on the characteristic relationship between temperature and the absorption/desorption pressures of an interstitial metal hydride, a simple but effective thermally driven hydrogen compressor can be built to supply at least 1000 bar for laboratory experiments. The compression ratio is proportional to the enthalpy of absorption, so that selecting an interstitial hydrogen storage alloy determines the achievable compression ratio between the available temperatures of heat supply and heat rejection. The characteristics of MH systems affecting the design and performance of a compressor (activation, pressure hysteresis, plateau slope, kinetics, cyclic lifetime) have been briefly discussed. The volume of a compressor needed to charge (itself and) an experiment volume to a desired pressure, and the required amount of hydrogen storage alloy, were also calculated. Candidate materials for the compressor pressure vessel were also discussed, particularly in relation to hydrogen embrittlement and mechanical strength. Other practical matters affecting performance and safety (seals, leak integrity, wall friction) were briefly discussed. Finally, two examples of compressor designs used in the authors’ laboratories were described: a manual purpose-built compressor for 1000 bar, and an automated 100-bar compressor assembled from readily available components.

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