

# Hydralloy C5 in single and coupled metal hydride systems for thermal applications in vehicles

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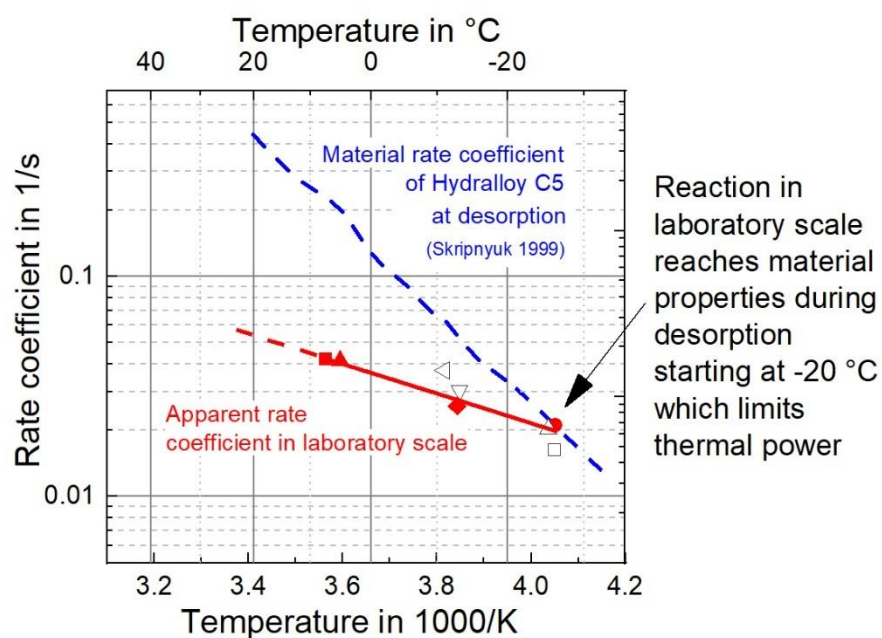
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## Keywords

Preheating; air conditioning; metal hydride; open and closed system; single and coupled reactions; vehicle applications

## Graphical Abstract

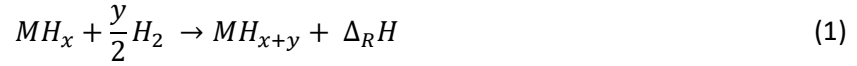


## Abstract

Hydralloy C5 ( $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Mn}_{1.46}\text{V}_{0.45}\text{Fe}_{0.09}$ ) is a very fast reacting metal hydride and is therefore investigated for two high thermal power applications in vehicles at room temperature and down to  $-20\text{ }^{\circ}\text{C}$ : preheating and air conditioning. The experimental findings in a  $\sim 1\text{ kg}$  of hydride material scale are evaluated with regard to their implications for potential technical systems. In order to preheat components, Hydralloy C5 can be used to supply hydrogen to  $\text{LaNi}_{4.85}\text{Al}_{0.15}$ , which then releases thermal energy at a high thermal power even from temperatures as low as  $-20\text{ }^{\circ}\text{C}$ . A main result is that, for the present reactor design, this coupled reaction shows a significant dependency of power on the ambient temperature. In fact, the reaction rate of Hydralloy C5 represents the main limitation on thermal power at low temperature. Nonetheless, the performance of at least  $0.5\text{ kW/kg}_{\text{MH}}$  allows the preheating of  $2\text{ L}$  of lubricant by  $20\text{ K}$  within  $120\text{ s}$  by  $2\text{ kg}$  of metal hydride in  $0.8\text{ L}$  of volume. For air conditioning, the endothermal hydrogen desorption performance of Hydralloy C5 was investigated at  $10$  to  $20\text{ }^{\circ}\text{C}$ . The experiments performed for the considered open system with external hydrogen supply and release show thermal mean powers of up to  $2\text{ kW/kg}_{\text{MH}}$ . Overall, it is shown that the desorption reaction between  $10$  and  $20\text{ }^{\circ}\text{C}$  is thermally limited in the considered reactor design. Based on the power achieved, less than  $4.5\text{ kg}$  of Hydralloy C5 would be sufficient to cover the air conditioning demand in conventional vehicles.

# 1. Introduction

Metal hydrides are metal alloys which react exo-/endothermally in a reversible reaction with hydrogen as given in Equation (1).



The absorption of hydrogen releases thermal energy (left to right) and desorption requires thermal energy and hence generates a cooling effect (right to left). There is an equilibrium correlation between the temperature level of the thermal energy and the pressure level of the hydrogen gas for every metal hydride alloy. The reaction is driven by either a temperature or a pressure difference. Hence, it can be used as a thermal storage material or as a converter of the potential energy of hydrogen pressure to thermal energy (heat or cold). With a rate coefficient of  $0.003 \text{ s}^{-1}$  at  $-20 \text{ }^\circ\text{C}$  [1], Hydralloy C5<sup>1</sup> ( $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Mn}_{1.46}\text{V}_{0.45}\text{Fe}_{0.09}$ ) is a very fast reacting metal hydride in the low temperature range and hence could meet the high thermal power demand in vehicle applications.

Therefore, the present work considers Hydralloy C5 for two relevant applications in vehicles: preheating of vehicle components and air conditioning of the cabin. Both require high thermal power at low temperature down to  $-20 \text{ }^\circ\text{C}$ . Surplus energy is to be used for the regeneration process in order to reduce emissions and increase efficiency in vehicles.

## 1.1. Preheating

Cold starting of an internal combustion engine is responsible for a lot of pollutants ( $\text{NO}_x$ , HC, VOC). Cipollone et al. [2] state that around 60 % of the harmful substances are produced before the engine is stabilized at operation temperature. Reiter et al. [3] indicate a proportion of as much as 80 %. As preheating the vehicle components of conventional vehicles shortens the start-up phase, it can reduce the emission of pollutants while the system is below operation temperature.

Various reasons for these cold start emissions were identified in the literature. For example, Andrews et al. [4] identify frictional losses by the high viscosity of a cold lubricant as a reason. Roberts et al. [5] additionally describe the effect of an inefficient catalyst below operation temperature and a cold combustions wall. The enriched fuel/air mixture during the cold start adds to the emissions, as described by Dardiotis et al. [6].

The assumed case in this work is preheating the lubricant. As described by Andrews et al. [4] and Roberts et al. [5], the effect of the lubricant is caused by the strong dependency of its viscosity on

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<sup>1</sup> Hydralloy C-materials are numbered according to their percentage of other components than titanium. Therefore,  $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Mn}_{1.46}\text{V}_{0.45}\text{Fe}_{0.09}$  – the material used in this study – is called Hydralloy C5.

temperature. High viscosity increases the pump work at increased pressure, frictional losses and engine wear and leads to decreased efficiency. Small temperature increases at low temperature result in a large reduction of viscosity. Hence, the first 20 K of heating can reduce it by 65 %, and even more for heating up to 20 °C. Therefore, a small temperature increase of the lubricant by a preheater can considerably reduce the friction and its effect on pollutants. Later on in the driving cycle, the lubricant reaches a temperature of 90 to 130 °C, which can be used for regeneration.

This work investigates a metal hydride preheater aiming at a modest temperature increase and run by the lubricant's waste heat. This application requires a fast heat supply in winter temperatures as low as -20 °C. Such a preheater has to provide the reaction partner hydrogen within the system. To reduce the volume and system pressure dramatically, instead of storing hydrogen in a pressurized tank it is stored in another metal hydride. Hence, two metal hydrides exchange hydrogen in coupled, strongly interdependent reactions which could dramatically affect the process and hence thermal power.

Some work has been published on heat storage with metal hydrides. Qin et al. investigated two LaNi-based materials for heat and cold production in a scale of 2.75 kg material [7]. At 20 °C they measured 0.48 kW/kg for heat generation and 0.25 kW/kg for cold generation. Park et al. also studied an LaNi-based material in a small-scale reactor (0.080 kg) at 30 °C, and the resulting thermal power could be extrapolated to 0.4 kW/kg [8]. Fang et al. developed a coupled system for heat and cold generation in electric vehicles based on  $\text{MgH}_2$  and Hydralloy C, reaching 6.4 kW/kg thermal peak power, when extrapolating from 0.050/0.190 kg of material [9]. However, their system requires a regeneration temperature of 390 °C. Furthermore, Liu et al. studied an open system with  $\text{LaNi}_5$  and 0.220 kg of material at temperatures between 20 and 60 °C for thermal energy storage [10].

All of these publications have in common that they aim at high thermal power output using metal hydrides. However, to the knowledge of the authors, no investigations have been published for heat generation at lower temperatures, e.g. below 0 °C, in particular for coupled reactions, other than the authors' own work. This previous work revealed that for coupled reactions the temperature level has the largest effect on thermal power and causes a decrease by over 60 % from 20 to -20 °C [11, 12]. The cause of the observed limitation at low temperatures, however, has not been identified so far. This question will be addressed in the first part of the present study with a focus on Hydralloy C5 as the hydrogen supplying material for preheating applications.

## 1.2. Air conditioning

Besides heat demand during start-up, there is also a need for continuous air conditioning of the vehicle cabin e.g. in summer. Whereas the heat demand could be supplied – at least theoretically - by the available waste heat from the fuel cell, the generation of cold requires mechanical work that has to be generated on board. If, however, cold could be at least partly generated by surplus energy, the energy consumption could be decreased, leading to a direct increase of the driving range as well as a reduced cost per driven distance.

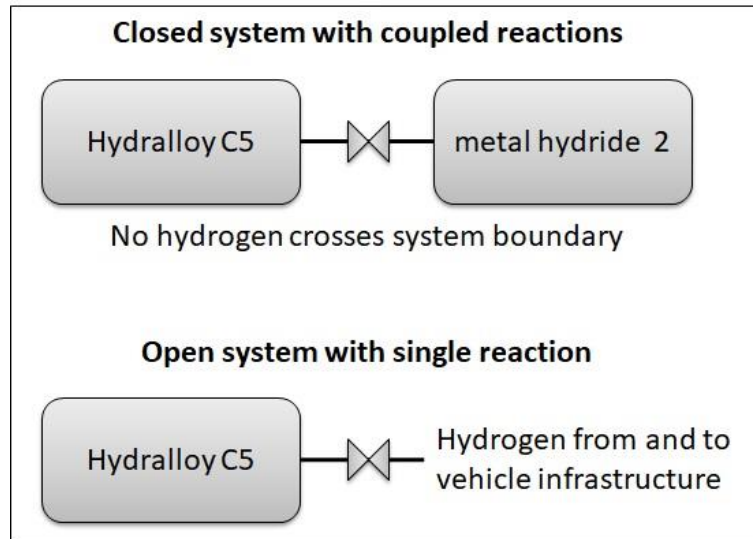
Looking at metal hydrides reacting reversibly with hydrogen, this work focuses on the application in fuel cell vehicles. In fact, the desorption reaction of Hydralloy C5 at a higher temperature and fast pressure change is investigated. Here, a single reaction of one metal hydride can be operated in a so-called open system, as hydrogen is available from the infrastructure at different pressure levels. The hydrogen tank can provide high pressure even if the tank is considered empty; in this case, it still contains hydrogen at 30 bar. Using this as the upper pressure level, the absorption can always be triggered. The low pressure of the fuel cell of around 2–6 bar can be used for the metal hydride desorption reaction. Until now, this available pressure difference has been unused, throttled and lost. This operation mode can use the unused pressure difference to drive a heat pump effect – both heat and cold are possible – without any hydrogen consumption.

By analogy to the preheating application introduced before, in theory it is also possible to use thermal energy to run a closed metal hydride system with two coupled reactions. This was investigated e.g. by Linder et al. [13] and Paya et al. [14]. However, the pressure change in an open system will definitely be faster than any pressure change that a second metal hydride could cause. Therefore, the present work focuses on the reaction performance that can be achieved in an open system in order to identify the potential and limits of the investigated material Hydralloy C5 for hydrogen supply at temperatures below 0 °C.

In the literature, some work has been published on air conditioning for single reactions. Using  $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$  and a hydrogen pressure of 50 bar, Linder and Kulenovic [15] reported a mean power of 1.1 kW/kg<sub>MH</sub>. More recently, Weckerle et al. [16, 17], from the same group as the authors of this paper, published work about a pressure-driven, open system for air conditioning. They used Hydralloy C2 in quasi-continuous operation and coupled to a PEM fuel cell. They reported a maximal thermal mean power of 276 kW/kg<sub>MH</sub> at an electric power of the fuel cell of 7 kW and a temperature of 20 °C. This database of the specific thermal cooling powers achieved will be extended by the present paper for another type of Hydralloy material (namely Hydralloy C5), in particular at lower temperatures.

### 1.3. Closed and open system

The two applications described are based on different operation modes (closed and open), depicted in Figure 1. The thermally driven closed system consists of two interdependent, coupled reactions. No hydrogen crosses the system boundary. On the other hand, the open system allows the unused pressure potential of the hydrogen tank in the fuel cell vehicles to be converted to thermal energy by a single reaction.



**Figure 1. Configuration of open and closed metal hydride system for thermal applications**

For continuous operation (cooling or heating), in one half-cycle one system generates cold while the other regenerates, and vice versa, whereas discharge and regeneration have to take place within the same time frame. As a result, two of the systems described are necessary and the required system size is doubled – two reactors for fuel cell vehicles operating as the open system and four reactors if no hydrogen infrastructure is available in closed systems, e.g. in cars with internal combustion engines.

Both the applications described require fast desorption of Hydralloy C5 at low temperatures. During pre-heating, Hydralloy C5 is the hydrogen supplying material and during air conditioning, Hydralloy C5 actually produces the cooling effect. Since this material is a very fast reacting metal hydride, its reaction is investigated in this paper as the key element for preheating and air conditioning in vehicles run by surplus energy. The results indicate the reachable specific power of metal hydride sorption systems in general.

In the first part of the present work, the desorption reaction down to -20 °C is investigated for the hydrogen supply in the preheating application. Different boundary conditions such as regeneration and heat transfer as well as material properties are taken into account. The open question is if a

temperature decrease of Hydralloy C5 during desorption in a large scale reduces the rate coefficient even of such a fast material in such a way that this material characteristic limits the thermal power output.

The second part investigates the desorption reaction for the cooling effect in air conditioning applications. The effect of the fast pressure change at temperatures between 10 and 20 °C is studied at different boundary conditions in order to show the present system's potential as well as the influences of temperature and heat transfer fluid mass flow on the resulting thermal power output.

## 2. Material and methods

### 2.1. Material properties

The Hydralloy C5 ( $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Mn}_{1.46}\text{V}_{0.45}\text{Fe}_{0.09}$ ) used for this study was supplied by GfE Metalle und Materialien GmbH (Germany). For the experiments in the closed preheater system additionally  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  from Konikindustries (China) was used. Both materials were characterized previously, and details can be found in [18].

The thermodynamic properties of Hydralloy C5 are given in Figure 2, including the boundary conditions for preheating with  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  and air conditioning with hydrogen from the vehicle infrastructure. Due to the comparatively strong dependence of the equilibrium pressure on hydrogen conversion (the plateau slope of desorption is  $0.53 \text{ wt.\%}^{-1}$  [18]), the exact values during reaction vary. For better illustration, the values are given here for 50% of hydrogen conversion.

At the lowest ambient temperature during preheating (red), Hydralloy C5 desorbs at around 1 bar to  $\text{LaNi}_{4.85}\text{Al}_{0.15}$ , which absorbs hydrogen at around 600 mbar at the initial temperature. At a regeneration temperature of 130 °C,  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  desorbs at 23 bar and Hydralloy C5 absorbs at ambient temperature. For air conditioning (blue), in order to generate cold at 15 °C, Hydralloy C5 has to desorb at pressures below 5 bar to the FC. Absorption at 30 bar results in an equilibrium temperature of ~ 55 °C, which allows a substantially large temperature difference with the summer ambient temperature of 35 °C.

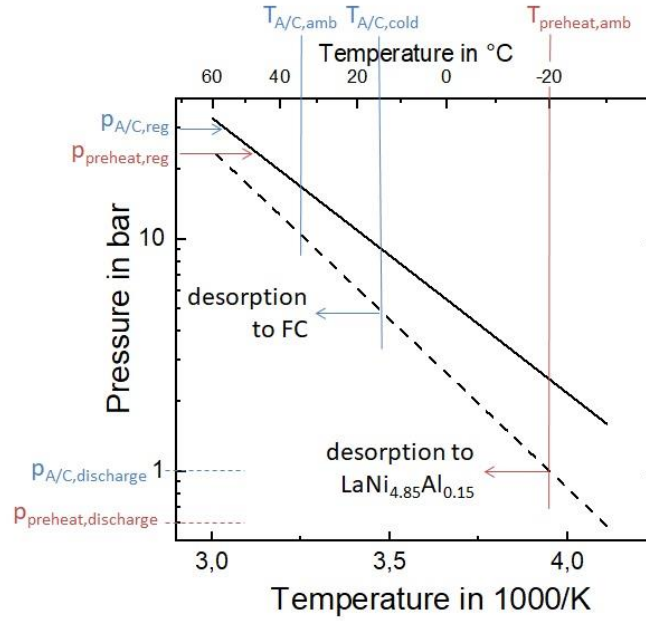
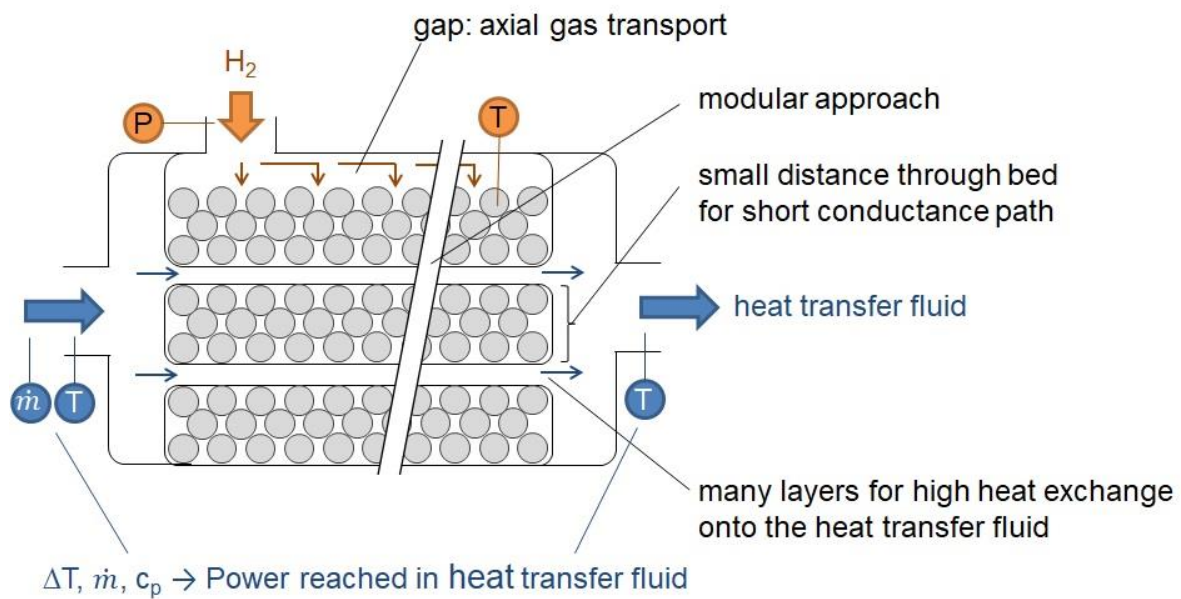


Figure 2. Thermodynamic properties of Hydralloy C5 from [18] (absorption: solid line, desorption: dashed line) including boundary conditions for preheating (red) and air conditioning (A/C, blue)

## 2.2. Reactor and test bench

Besides a fast reacting material with thermodynamics fitting the temperature and pressure conditions in vehicles, a high thermal power reactor is necessary in order to extract the thermal energy as fast as possible and thereby minimize the system in total. This requires sufficient gas transport as well as heat transfer through the material. For unmodified materials, short distances for heat conduction are required. Figure 3 shows the main dimensioning aspects for a reactor with indirect heat transfer. The metal hydride is positioned on one side and the heat transfer fluid flows on the other side (in this case inside the tubes). With a gap at the top, the hydrogen can flow freely along the reactor's length and the pressure loss is determined only by the bed width. This allows a modular approach in the axial direction. More layers and a smaller layer thickness increase the heat transfer area and reduce the distance for heat transfer. On the other hand, this also increases the passive reactor mass. The thermal power transferred to the heat transfer fluid can be calculated from its mass flow  $\dot{m}$ , heat capacity  $c_p$  and temperature change  $\Delta T$ .





**Figure 3. Schematic design of a high thermal power reactor**

In this study, a tube bundle heat exchanger ensuring excellent heat and mass transfer is used as the reactor and a cross-sectional schematic is displayed in Table 1, right. The metal hydride is positioned on the shell side and the heat transfer fluid absorbs or provides heat on the tube side. One reactor is filled with 615 g of Hydralloy C5 and for the closed system another one is filled with 960 g of  $LaNi_{4.85}Al_{0.15}$ . The gas has to cover a maximal distance of 38 mm (shell diameter) and heat is transferred through the material to the tubes at a maximal distance of around 1 mm. The details of the reactor are summarized in Table 1.

**Table 1. Details of tube bundle reactor and cross-sectional schematic**

Total length, mm	565	
Shell side length, mm	508	
Shell side inner diameter, mm	38	
Empty weight empty, kg	2.09	
Tube count, -	91	
Tube outer diameter, mm	2.4	
Heat transfer area, m <sup>2</sup>	0.34	
Maximal pressure tube side, bar	83	
Maximal pressure shell side, bar	55	
Maximal temperature, °C	425	

The test bench is depicted in Figure 4. It can provide a temperature range of the heat transfer fluid of -20 to over 130 °C and as heat transfer fluid SiOil M40.165/220.10 by Huber Kältemaschinenbau AG (Germany) is used. Furthermore, hydrogen can be supplied at pressures up to 30 bar. The considered thermal power transferred to the heat transfer fluid is measured by thermocouples and

mass flow meters and considers all losses of thermal ballast and to the ambient. It is calculated according to Equation (2). The probable error in the thermal power obtained was less than  $\pm 11\%$  with the main influence of the determination of the heat capacity with  $\pm 10\%$  [12]. With the thermal power values over time, the hydrogen conversion  $\omega$  is calculated taking the reaction enthalpy  $\Delta H$  and metal hydride mass  $m_{MH}$  into account; see Equation (3), where  $t = N \cdot \Delta t$ .

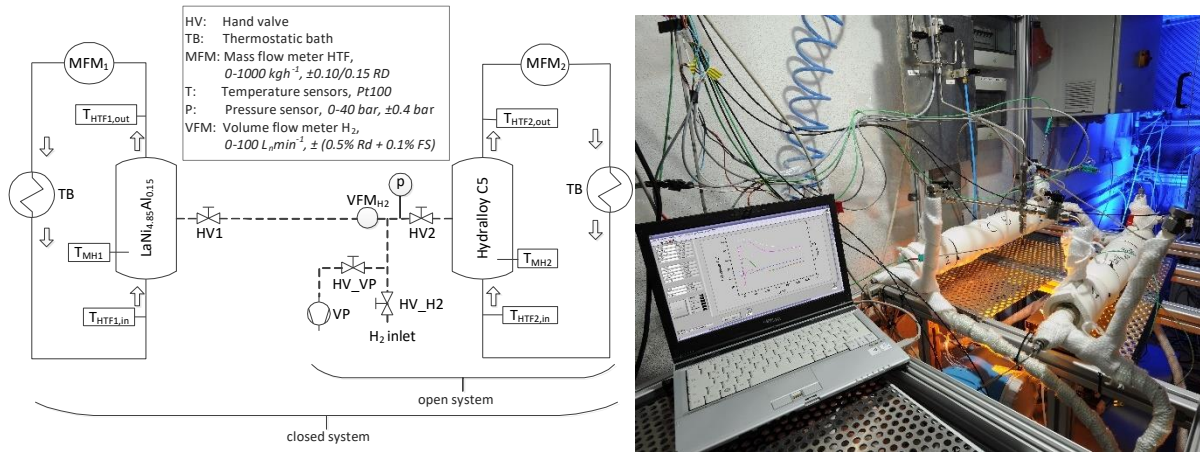
$$P(t) = \dot{m}_{HTF}(t) c_p(t) (T_{out}(t) - T_{in}(t)) \quad (2)$$

$$\omega(t) = \frac{\sum_0^N (P(t) \Delta t)}{\frac{\Delta H m_{MH}}{100 M_{H_2}}} \quad (3)$$

For discussion of the reaction rates achieved, the transient behavior of the transformed fraction is specified instead of the hydrogen conversion  $\omega$ . This transformed fraction  $x$  is calculated for each experiment as:

$$x(t) = \frac{\omega(t)}{\omega_{\max, \exp}} \quad (4)$$

The setup of the reactor and test bench was used in the previous work of the authors [11, 12] and some details on the instruments used are indicated in Figure 4. For more details, the reader is referred to the previous publications.



**Figure 4. Schematic of experimental setup and photograph of the setup including the two reactors**

## 2.3. Experimental conditions

### 2.3.1. Preheating

For the preheating case, the required metal hydride mass results from the thermal energy needed for the vehicle component. Heating a part of the lubricant of e.g. 2 L by 20 K in order to minimize the most negative effects due to viscosity would require 120 kJ, according to Kunze et al. [19]. Around 150 kJ can be stored in 960 g of  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  with an absorption reaction enthalpy of 31 kJ/mol and hydrogen conversion of 1 wt.-% [18]. This mass is used in this study and considered as a relevant scale.

Heat generation is required as fast as possible, while regeneration may take all the residual time of the driving cycle after start-up. The peak thermal power is the performance indicator considered. Additionally, the different reaction times for reverse and forward reaction influence the material choice, allowing the equilibrium of the heat generation material to be closer to regeneration conditions.

Winter ambient temperatures of -20 to 20 °C and regeneration temperatures of 90 to 130 °C are considered. Both reactors are adjusted to the assumed ambient temperature and discharge is triggered by opening the separating valve. The overall pressure is measured in the tube connection between the reactors. From the temperature and mass flow of the heat transfer fluid, the thermal power is calculated according to Equation (2). After the reaction, the valve is closed and the  $\text{LaNi}_{4.85}\text{Al}_{0.15}$ -reactor is adjusted to the considered regeneration temperature. Once at steady state, the valve is opened again. Now, the reverse reaction can take place and the absorption heat of Hydralloy C5 is released at ambient temperature level.

In order to investigate the influence of the Hydralloy C5 desorption reaction on the thermal power, one experiment for each condition was chosen from [11]. Additionally, experiments on the single reaction of Hydralloy C5 were performed. At an ambient temperature of 20 °C,  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  absorbs at a mid-plateau pressure of around 1 bar, which was used as the desorption pressure for Hydralloy C5. Details are given in Table 2.

**Table 2. Experimental conditions of the preheating experiments**

Coupled reactions at preheating conditions				
No. of experiment*	T <sub>amb</sub> in °C	T <sub>reg</sub> in °C	$\dot{m}_{\text{HTF}}$ in kg/h	
12	-20	130	150	
10			250	
7				
6				
4				
3				
5	0	130	250	
1		110		
9		90		
5	20	130	150	
1			250	
9			425	
Single reaction of Hydralloy C5 at preheating conditions				
No. of experiment	T <sub>amb</sub> in °C	p <sub>abs</sub> in bar	p <sub>des</sub> in bar	$\dot{m}_{\text{HTF}}$ in kg/h
A, B	20	30	1	250

\*numbered according to [11]

The main goal is to identify limitations in the thermal power output at various conditions, since this is the most important parameter for preheating applications. They can be caused by heat transfer, mass transfer or reaction kinetics. Therefore, the reaction rates of the materials have to be considered. The overall reaction rate is affected by a temperature-dependent rate coefficient  $k(T)$ , a pressure dependence function  $f(p)$  and the reaction mechanism  $F(x)$ . The single terms were defined and discussed in [18] and an equation to fit the reaction rate coefficient from experimental data was derived as given in Equation (5). Thermodynamic data of the material is required for the calculation of  $f(p)$  and  $F(x)$ . From data at different temperatures, the pre-exponential factor  $A$  and the activation energy  $E_a$  can be fitted (see Equation (6)).

$$\frac{F(x)}{f(p)} = \frac{-\ln(1-x)}{\frac{|p_{eq}-p|}{p_{eq}}} = k(T) \cdot t \quad (5)$$

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

### 2.3.2. Air conditioning

The second part of this paper investigates the performance of Hydralloy C5 at conditions for cold generation in a single, open reaction. Cold is to be generated at 10, 15 and 20 °C. For regeneration (the absorption process), ambient temperatures occurring on a hot summer day have been considered as 35 °C. The reference flow rate of the heat transfer fluid was 340 kg/h (~ 6 L/min), similar to vehicle systems as also investigated by Weckerle et al. in [16].

The desorption pressure is set to 1 bar at the desired cold generation temperature. Regeneration takes place at 35 °C and a pressure of 30 bar. At this pressure, the pressure tank in a fuel cell vehicle is considered empty; hence the air conditioning system can always be operated in these conditions. Details are given in Table 3.

**Table 3. Experimental conditions of the air conditioning experiments**

No. of experiment	$T_{\text{cold}}$ in °C	$\dot{m}_{\text{HTF}}$ in kg/h
II	10	340
I, IV, VIII, IX	15	
V	20	250
III		340
VI, VII		425

For constant cooling, two identical systems would have to be operated quasi-continuously. While one system generates cold during one half-cycle, the other one is regenerated and vice versa. This would include the effect of the temperature change of the reactors on the thermal mean power. This, however, is not included in this study since only one reactor is operated and the reaction is triggered after the change of temperature. Hence, the whole effect of the reaction is represented in the mean thermal power value. For air conditioning, the mean thermal cooling power within one half-cycle time is the value of interest. It is calculated by dividing the thermal energy released according to Equation (3) during the half-cycle time by that time. The half-cycle time and thermal power define the amount of metal hydride. Here, a half-cycle time of 60 s is chosen and a maximal thermal mean power of 2 kW is assumed. This requires around 575 g of Hydralloy C5 ( $\Delta h_{\text{C5,des}} = 27.8 \text{ kJ/mol}$ ,  $\omega = 1.5 \text{ wt.-%}$  [18]), hence the mass of 615 g used can supply enough energy for the intended experiments.

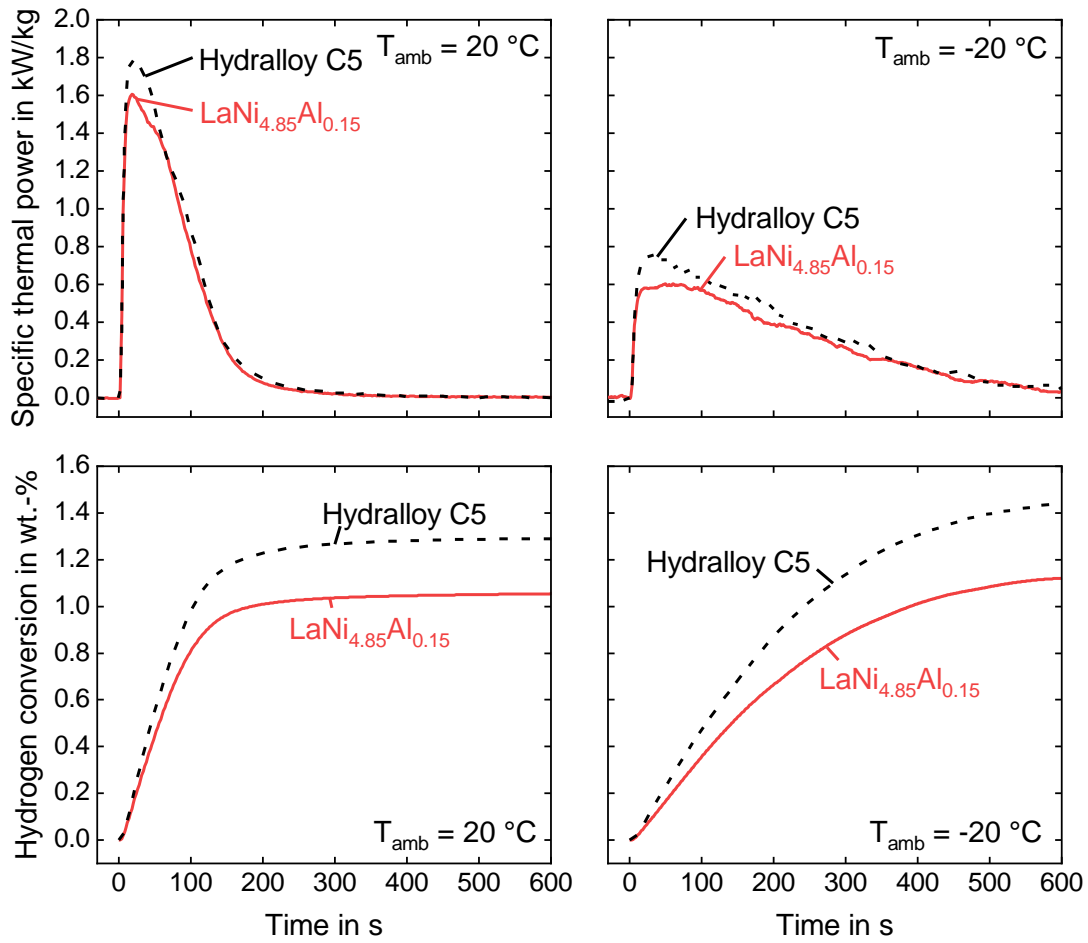
### 3. Results and discussion

This section presents the results for Hydralloy C5 in preheating and air conditioning systems. For preheating, the peak power that can be reached is of interest for fast heat-up. In contrast, for air conditioning, it is the mean cooling power that can be reached in continuous operation that is of interest. In both scenarios the desorption of Hydralloy C5 is the critical step, because low pressure reduces gas transport and low temperature reduces the reaction rate.

#### 3.1. Coupled reactions for preheating in closed system at low temperature

Hydralloy C5 was previously investigated in a coupled reaction with  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  in [11]. The underlying reason for the observed decrease in power of over 60 % for a temperature decrease from 20 to -20 °C is investigated in this section.

For the coupled reactions of Hydralloy C5 and  $\text{LaNi}_{4.85}\text{Al}_{0.15}$ , an example of the thermal power and hydrogen conversion for both metal hydrides is shown in Figure 5 for an ambient temperature of 20 and -20 °C. For better comparison, all thermal power and hydrogen conversion results are shown as positive, although Hydralloy C5 desorbs and causes a temperature decrease. The specific thermal power of Hydralloy C5 reaches higher specific values than  $\text{LaNi}_{4.85}\text{Al}_{0.15}$ , because less metal hydride mass is necessary due to its higher hydrogen conversion capacity (see Figure 5, bottom), although the desorption enthalpy of Hydralloy C5 is slightly lower than the one for absorption of  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  ( $\Delta_{\text{R}}H_{\text{C5,des}} = 27.8 \text{ kJ/mol}$ ,  $\Delta_{\text{R}}H_{\text{LaNi}_{4.85}\text{Al}_{0.15,abs}} = 31.0 \text{ kJ/mol}$  [18]). Besides that, the course of both materials is very similar because the coupled reactions are strongly interdependent. Hydralloy C5 reaches a peak thermal power of 0.76 kW/kg<sub>MH</sub> at -20 °C and 1.79 kW/kg<sub>MH</sub> at 20 °C. It has to be mentioned at this point that the overall capacity of both materials after 600 s increases slightly, e.g. from ~1.3 wt.-% at 20 °C to 1.45 wt.-% at -20°C. This behavior is common for all metal hydrides and is caused by the increasing width of the plateau in the PCIs with decreasing temperature.



**Figure 5.** Performance of both materials in the coupled reactions at 20 and  $-20\text{ }^{\circ}\text{C}$  (partly from [1]; #1, 10), regeneration at  $130\text{ }^{\circ}\text{C}$

The same is true for all the conditions investigated for the coupled reactions: The course of thermal power and of hydrogen conversion is very similar, with slightly higher values for Hydralloy C5. The specific thermal peak power values reached for Hydralloy C5 are given in Figure 6 for all the conditions investigated (cf. Table 2).

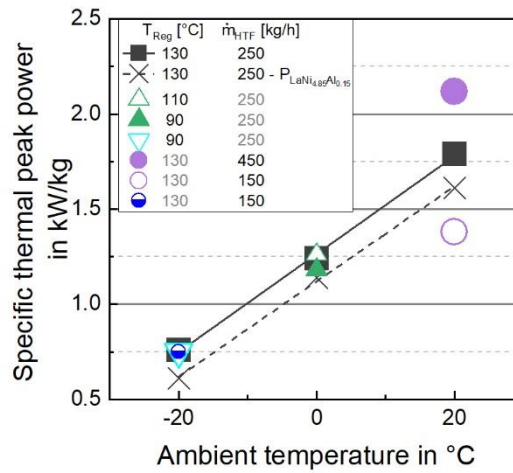


Figure 6. Specific thermal power for all preheating experiments

The strong dependency on the ambient temperature can be seen clearly (black full squares, solid line). The thermal power has more than doubled from -20 to 20 °C. Since both reactions are coupled, the same trend can be observed for  $\text{LaNi}_{4.85}\text{Al}_{0.15}$ , which is actually causing the “heating” effect in the final system. Its values are also included for the temperature variation (black crosses, dashed line, cf. [11]).

The effect of the regeneration temperature is much smaller. A slight increase of thermal power at 0 °C can be observed, from 1.18 kW/kg<sub>MH</sub> for 90 °C to almost the same values for both 110 and 130 °C of 1.26 and 1.24 kW/kg<sub>MH</sub>, respectively (green triangles). No effect can be seen at -20 °C (cyan open reverse triangle). This can be explained by a fixed temperature difference for a specific metal hydride pair which has to be overcome for full conversion, independent of the temperature level. For the given pair, this temperature difference is around  $\Delta T = 110$  K. Therefore, conversion is incomplete for  $\Delta T = 90$  K ( $T_{\text{reg}} = 90$  °C for  $T_{\text{amb}} = 0$  °C), leading to a slightly smaller thermal power value, whereas full conversion is reached in all other cases ( $T_{\text{reg}} \geq 90$  °C for  $T_{\text{amb}} = -20$  °C;  $T_{\text{reg}} \geq 110$  °C for  $T_{\text{amb}} = 0$  °C) [11].

The effect of higher mass flow of the heat transfer fluid can only be seen at a high ambient temperature. At 20 °C, a peak power of 2.12 kW/kg<sub>MH</sub> was obtained for a mass flow of 425 kg/h. This value decreases to 1.79 and 1.38 kW/kg<sub>MH</sub> for a mass flow of 250 and 150 kg/h, respectively (violet circles). A decrease in mass flow at -20 °C does not change the resulting power (blue half-open circle). Hence, the reactions seem to be limited by heat transfer for a high ambient temperature; however, this limitation can be excluded at low temperatures.



From this discussion, neither the regeneration temperature and hence incomplete conversion nor the mass flow rate and hence heat transfer limitations could be identified for the substantially lower thermal power values at low ambient temperatures.

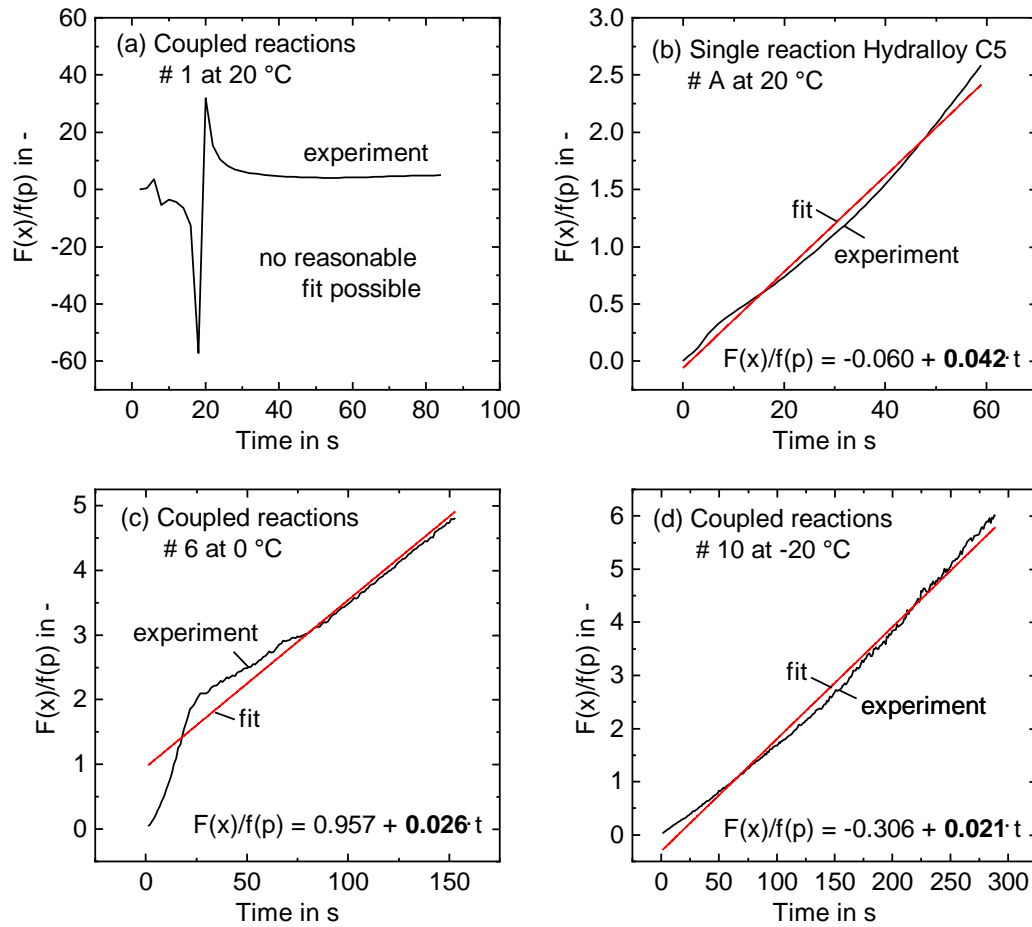
From these conclusions the question arises: does the temperature decrease of Hydralloy C5 during desorption on a large scale reduce the rate coefficient even of such a fast material in such a way that this material characteristics limit the final thermal power output?

By analogy to the procedure for intrinsic material characterizations, a resulting straight line of Equation (5) would allow the conclusion that a single rate coefficient  $k$  is the time-determining property for the investigated temperature. Hence, for the present lab-scale experiments an apparent rate coefficient  $k_{ap}$  for the large-scale experiment could be derived. If this is possible for several temperatures and these  $k_{ap}$  additionally fall on one line, it could be assumed that the limiting factor of the thermal power is in fact the materials' reaction rate, and an apparent pre-exponential factor  $A$  and activation energy  $E_a$  could be derived according to Equation (6). This analysis was performed with the laboratory-scale experiments and is explained in the following.

Exemplary fits of the reaction rate for each temperature are given in Figure 7. The findings are coherent for all the coupled experiments. For the coupled reactions at 20 °C (Figure 7, a), no fit was possible. Consequently, it can be assumed that the process observed is not limited and hence not described correctly by the kinetic correlation. This observation fits the conclusions from Figure 6, where the thermal power at high ambient temperature was found to be limited by heat transfer to the heat transfer fluid.

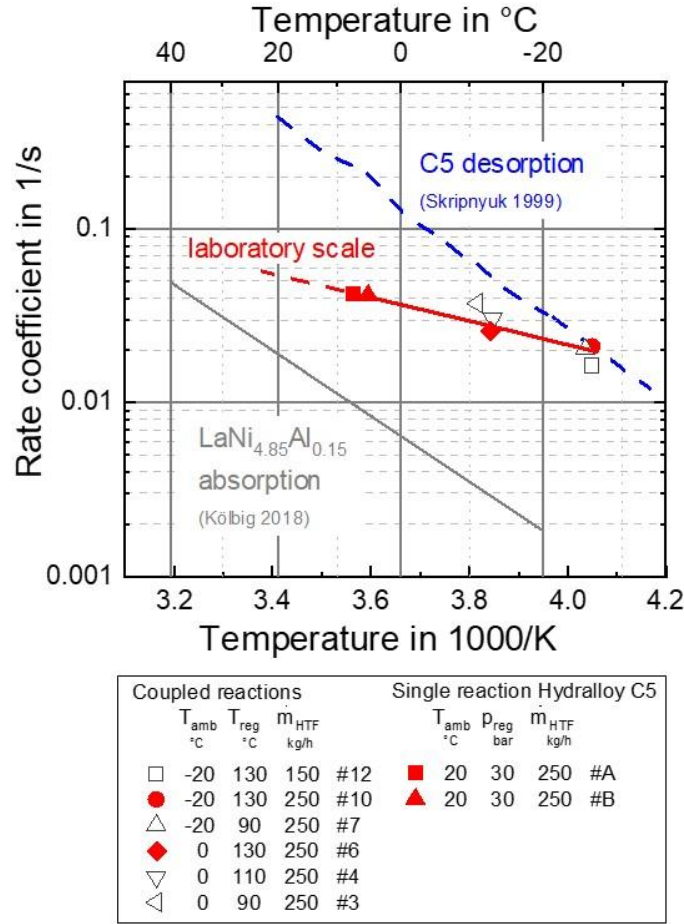
Additional single reaction experiments for Hydralloy C5 were performed at 20 °C in order to investigate the material limitations thoroughly: desorption to ambient at a constant pressure of 1 bar uncouples the desorption reaction from the absorption one. High thermal peak power values of 2.33 and 2.32 kW/kg<sub>MH</sub> are obtained for experiments A and B, respectively. The results also allowed a fit of Equation (5) (see Figure 7, b). The fit yielded a coefficient of determination of 98.2 %. Therefore, at 20 °C, the single reaction is limited by the material's kinetics, whereas the coupled reactions are thermally limited.

For the coupled reactions at 0 and -20 °C, a fit was possible too (Figure 7, c and d). The fit for -20 °C yielded a close match, with a coefficient of determination of 99.3 %, whereas for 0 °C, the fit only revealed a coefficient of determination of 94.1 %. This can also be observed in the diagram, where the line from the experiment shows a discontinuity. Therefore, limitations other than the reaction rate might overlap and also influence the reaction rate in the large-scale experiments at 0 °C.



**Figure 7. Approximated kinetic fits of laboratory-scale experiments**

Concluding, the experiments of the coupled reactions at -20 and 0 °C and the single reaction of Hydralloy C5 at 20 °C can be described correctly by the correlation of the reaction rate. The resulting apparent reaction rate coefficients for all experiments are given in Figure 8. The values are depicted at the average material temperature during reaction. The intrinsic rate coefficients of the materials are also included.



**Figure 8.** Apparent rate coefficients of the coupled and single reactions of Hydralloy C5 and the rate coefficient of  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  [18] and Hydralloy C5 [1]

For different experimental conditions, small variations for the apparent rate coefficient can be seen. With respect to the ambient temperature, a trend of increasing values for increasing temperature is obvious. The results for the single reaction fit this trend. Therefore, for the reaction in this specific reactor an apparent rate coefficient  $k_{ap}(T)$  can be defined. Neglecting variations other than the initial reaction temperature by using only experiments # 10, 6, A and B (full symbols), an apparent Arrhenius correlation (Equation (6)) can be derived to  $A = 10.81 \text{ s}^{-1}$  and  $E_a = 12,923 \frac{\text{J}}{\text{mol}}$  with a coefficient of determination of 98.4 %; see Equation (7), red line in Figure 8:

$$k_{ap}(T) = 10.8 \frac{1}{\text{s}} \cdot \exp\left(\frac{-12.9 \frac{\text{kJ}}{\text{mol}}}{RT}\right) \quad (7)$$

The properties of the pure materials show that  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  has a smaller rate coefficient than Hydralloy C5 at the same temperature and hence lower reaction kinetics. However, the absorption of  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  during preheating is self-accelerating, as the absorption heat leads to a temperature

increase. Hence, the rate coefficient increases. This effect was shown for the single reaction of  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  in [11]. In contrast, Hydralloy C5 has to desorb to supply hydrogen, which lowers the materials' temperature and therefore the rate coefficient.

For the initial temperature of  $-20\text{ }^{\circ}\text{C}$ , the temperature of Hydralloy C5 decreases to around  $-26\text{ }^{\circ}\text{C}$  in all cases, where the resulting apparent rate coefficients fall on the line with the pure material property. This indicates that the desorption reaction is kinetically limited, because the laboratory-scale reactions already reach the rate coefficient of the pure material. This value could only be increased if this already small temperature drop of Hydralloy C5 could be further reduced. This would, however, demand an even better reactor in terms of heat transfer, which might not be realistic for any mobile application due to volume, weight and most likely also cost constraints.

From this discussion it is concluded that, for preheating at low temperatures, the reaction rate of Hydralloy C5 is the crucial factor of the coupled reactions. Therefore, the ambient temperature plays a very important role for the performance of a closed metal hydride preheater even with a very fast material such as Hydralloy C5. Even with an ideal reactor design enabling isothermal desorption, the increase in thermal power is limited by the ambient temperature with the materials available today. This limitation has to be considered for future applications of coupled metal hydrides in vehicles.

Nonetheless, the given performance of the preheater allows quite realistic dimensions of the preheater. Heating a part of the lubricant, e.g. 2 L, by 20 K in order to minimize the most negative effects due to viscosity would require 120 kJ [19]. With the thermal power shown of more than  $0.5\text{ kW/kg}_{\text{MH}}$  based on the pre-heating material  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  (cf. Figure 6), 2 kg of metal hydride would take 120 s for heating the lubricant. With a bulk density of at least  $2500\text{ kg/m}^3$ , this results in a volume of only 0.8 L. This shows the still great technical potential of metal hydride based preheating that is able to deliver emission-free thermal energy on demand.

### **3.2. Single reaction for cooling effect in air conditioning application**

As described above, the desorption of Hydralloy C5 at very low temperatures is limiting the thermal power that can be reached. This section presents the results of single reaction experiments for the air conditioning application. In this case, the desorption is required at higher temperatures. As shown above, at these temperatures, the reaction rate of Hydralloy C5 does not dominate the reactor dynamics. The following chapter therefore gives an idea of the utilization potential of Hydralloy C5 in a high thermal power application.

The mean thermal power values within 60 s for all the air conditioning experiments performed are given in Figure 9. Thermal mean power values of 1.56 kW/kg<sub>MH</sub> at 10 °C, 1.72 kW/kg<sub>MH</sub> at 15 °C and 1.90 kW/kg<sub>MH</sub> at 20 °C are observed for experiments # II, IX and III, respectively. For the same conditions, the results lie very close together (open triangles, solid line).

The thermodynamic desorption pressure of Hydralloy C5 increases intrinsically with the increasing cold generation temperature. The hydrogen release pressure set for the desorption experiments remains unchanged at ambient pressure. Hence, the pressure difference increases, resulting in the obvious increase in thermal power.

At 20 °C, additionally, the mass flow of the heat transfer fluid was varied (red circle and squares). The thermal mean power for a mass flow of 425 kg/h varies slightly between 1.96 and 2.07 kW/kg<sub>MH</sub>. This is due to the different cooling performance of the thermostatic bath at this high thermal power. However, the peak values of these experiments are quite close, at 2.64 and 2.68 kW/kg<sub>MH</sub> compared to 2.46 kW/kg<sub>MH</sub> at 340 kg/h. The lower mass flow of 250 kg/h leads to a mean thermal power value of 1.74 kW/kg<sub>MH</sub>.

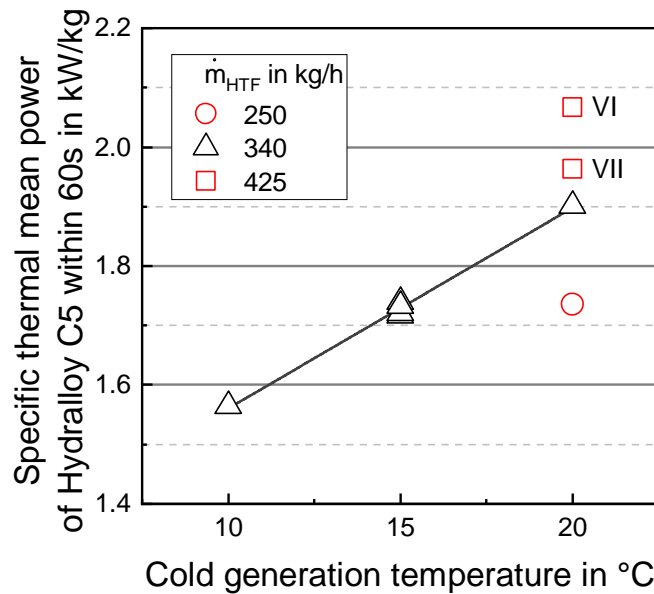


Figure 9. Specific thermal power of Hydralloy C5 for cooling experiments

Concluding, it can be stated that the thermal power in cold generation conditions for the desorption reaction of Hydralloy C5 is strongly dependent on the driving pressure difference, which is determined by the cold generation temperature and the desorption pressure to an FC. The thermal power increases for a higher cold generation temperature or lower desorption pressure. Additionally,

even at high thermal power at 20 °C, an increase of the HTF mass flow and hence an increase in heat transfer leads to faster reaction.

Therefore, in contrast to the preheating case, the desorption reaction here is limited thermally and not kinetically. This could be expected, as at the cold generation temperatures investigated, which are higher by 30 K and more, the respective reaction rate for Hydralloy C5 is higher by an order of magnitude (cf. Figure 8). As already discussed for the preheating experiments, the reactor design shows considerably high thermal power and further improvement would probably lead to substantially increased costs and weight.

The thermal power required for air conditioning in vehicles is higher than that shown for the reactors of this study, with reported values between 3.5 kW [20] and 7 kW [21]. To cover the upper limit of the whole demand with metal hydrides, around 3.7 to 4.4 kg of Hydralloy C5 would be needed, depending on the cold generation temperature required. This would be possible with modular design of the reactors. However, as in this case the reaction rate of Hydralloy C5 is not limiting, the mass specific power levels can be further increased by means of improved reactor design.

## 4. Conclusions

Hydralloy C5 is a fast reacting metal hydride and was therefore investigated for two high thermal power applications in vehicles: preheating and air conditioning. In both applications, the endothermic desorption of hydrogen from the Hydralloy C5 is the crucial step, either for hydrogen supply at the required pressure or for cold generation at the desired temperature.

As the hydrogen supply material in the coupled reaction with  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  for preheating, a significant dependency of power on the ambient temperature was shown. The peak thermal power of Hydralloy C5 was  $0.76 \text{ kW/kg}_{\text{MH}}$  at  $-20^\circ\text{C}$  and  $1.79 \text{ kW/kg}_{\text{MH}}$  at  $20^\circ\text{C}$ . The single reaction reached  $2.3 \text{ kW/kg}_{\text{MH}}$  at  $20^\circ\text{C}$ . Other boundary conditions investigated such as regeneration and heat transfer show significantly less effect on the thermal power than the ambient temperature. Although using a very fast reacting material, it could be shown that the reaction rate of Hydralloy C5 represents the main limitation on thermal power at such low temperatures. Nonetheless, the resulting thermal power released in the connected  $\text{LaNi}_{4.85}\text{Al}_{0.15}$  material of  $0.61 \text{ kW/kg}_{\text{MH}}$  at  $-20^\circ\text{C}$ , allows the preheating of 2 L of lubricant by 20 K within 120 s by 2 kg of metal hydride in 0.8 L of volume.

The desorption reaction of Hydralloy C5 was additionally investigated at higher temperatures for air conditioning and fast pressure change in an open system considered for FC vehicles. The experiments showed high mean thermal power values of  $1.6$  to  $1.9 \text{ kW/kg}_{\text{MH}}$  between  $10$  and  $20^\circ\text{C}$ . It increases at higher temperature due to the increased driving pressure difference. Increased heat transfer leads to even higher values of up to  $2.1 \text{ kW/kg}_{\text{MH}}$ . Hence, besides the pressure difference, although a high thermal power reactor was used, the desorption reaction between  $10$  and  $20^\circ\text{C}$  is still thermally limited. In order to reach the thermal power of conventional air conditioning systems of  $7 \text{ kW}$ , less than  $4.5 \text{ kg}$  of Hydralloy C5 would be required.

Based on the experimental investigations in this work, it can be concluded that, in general, the rate of reaction of Hydralloy C5 is extremely fast and clearly gives room for reactor improvements regarding weight specific power. However, since an endothermic desorption necessarily reduces the material's reaction temperature, e.g. hydrogen supply at very low reaction temperatures, the intrinsic material reaction rate will dominate the overall system dynamics. For such high power applications at ambient temperatures below  $-20^\circ\text{C}$ , an even faster metal hydride is required if higher weight specific power levels are necessary.

## Acknowledgments

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## Nomenclature

A	Pre-exponential factor	$s^{-1}$
$c_p$	Heat capacity	J/(gK)
$E_a$	Activation energy	J/mol
$f(p)$	Pressure dependence function	-
$F(x)$	Integral of reaction mechanism	-
k	Reaction rate coefficient	$s^{-1}$
$M_{H_2}$	Molar mass	g/mol
m	Mass	g
$\dot{m}$	Mass flow rate	kg/h
N	Number of time intervals	-
P	Thermal power	kW
p	Pressure	bar
Q	Thermal energy	kJ
R	Universal gas constant	J/(mol K)
T	Temperature	°C
$\Delta T$	Temperature gradient	K
t	Time	s
$\Delta t$	Time interval	s
x	Transformed fraction	1
$\Delta_R H$	Reaction enthalpy	kJ/mol
$\omega$	Hydrogen conversion	wt.-%



## Abbreviations

FC	Fuel cell
H <sub>2</sub>	Hydrogen
HC	Hydrocarbons
NO <sub>x</sub>	Nitrogen oxides
VOC	Volatile organic compounds

## Indices

abs	Absorption
amb	Ambient level
ap	Apparent
cold	Cold generation level
des	Desorption
eq	Equilibrium
HTF	Heat transfer fluid
max,exp	Maximum value in experiment
MH	Metal hydride
reg	Regeneration level

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