# Absorption storage of hydrogen in alloys of Ti, Ni, Mn, C

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***Abstract*—** *Hydrogen storage is considered one of the most critical issues that must be resolved for the implementation of economic and viable hydrogen energy systems. Without effective storage systems, it will be very difficult to achieve beneficial value from the hydrogen economy. One physical limit on the storage of hydrogen is the density of compressed and liquid hydrogen. Currently, considerable attention is being paid to the development of metal hydride alloys, which can effectively absorb and retain a large amount of hydrogen through chemical bonds. The article analyzes research into metal hydride alloys based on Ti-Cr-Mn, Ti-Cr-Ni and Cr-Ti-Ni0.5-Mn0.5.*

***Keywords*— hydrogen, metal hydride, absorption storage, storage capacity.**

## I. INTRODUCTION

At present, the world is paying close attention to reducing its energy dependence on oil and gas. Reducing the emission load due to the combustion of fuels is also a major issue that needs to be addressed. One possible solution to these problems is the use of renewable sources to produce hydrogen. Its use for energy purposes has no negative impact on the environment. A major problem in the implementation of hydrogen technologies in the energy sector is precisely the storage of hydrogen. Therefore if hydrogen is to be used as an ecological fuel in the future, it is necessary to create inexpensive and safe ways to store it.

Hydrogen produces metal hydrides with certain metals and alloys, which in some cases are of higher density than storage in a pressure or cryogenic vessel. Storage in metal hydride is a form of storage that is safer and more effective in terms of volume. We distinguish two possible methods of hydration of metals, direct chemical sorption and the reaction for the electrochemical splitting according to [1]:

$$M + \frac{x}{2}H_2 \leftrightarrow MH_x \tag{1}$$

$$M + \frac{x}{2}H_2O + \frac{x}{2}e \leftrightarrow MH_x + \frac{x}{2}OH \tag{2}$$

Metal hydride is formed by the host mesh of metal and water atoms. Metal and water create two different types of hydrides, α-phase if only part of the hydrogen is absorbed and β-phase if the metal is fully saturated with hydrogen.

Research into intermetallic alloys for hydrogen storage began about 20 years ago. The discovery of the absorption of hydrogen into intermetallic alloys opened up new opportunities for industrial development. Due to their high mass and therefore a small percentage by weight of hydrogen storage they remained unavailable for use in mobile applications.

Among the basic types of intermetallic alloys for storing hydrogen on the basis of their crystalline structure:

- AB2 - Laves phases
- AB5
- BCC - Body Centred Cubic, titanium-based alloy with centred cubic mesh.

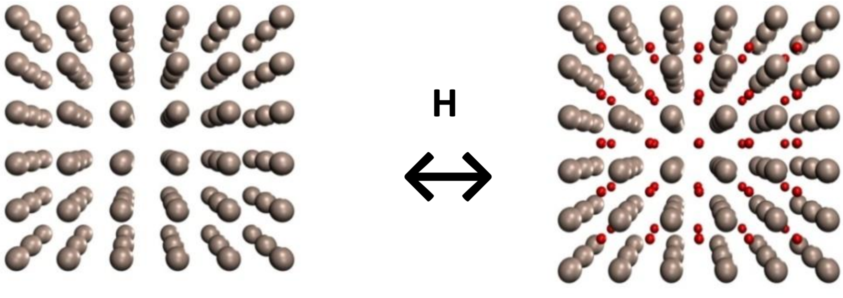



**FIG. 1 DEPICTION OF THE BASIC PRINCIPLE OF FUNCTIONING OF INTERMETALLIC HYDRIDES**

Intermetallic hydrides are often made up of a combination of the member constituting the stable hydride with members forming unstable hydrides. The process of hydration of metal itself is accompanied, in contrast to chemical bonding, by diffusion of hydrogen into the metal lattice or alloy (Figure 1). A major drawback of these materials is their low energy density per unit weight of metal.

## II. PREPARATION AND COMPOSITION OF MATERIALS FOR ABSORPTION STORAGE OF HYDROGEN

The initial step towards measuring the absorption properties is to prepare metal hydride alloys. The preparation and composition of the metal hydride alloys is the key to its storage properties. Among the various types of metal hydride alloys type AB2 alloy of Cr-Ti are among the most promising because of its relatively high desorption pressure, greater storage capacity and faster kinetics of the process.

To manufacture suitable alloys it was necessary to acquire powdered metal, from which the individual alloys are produced. The core element of each alloy is titanium with a grain size of 44 µm and a purity of 99%. Another important element is chromium; the grain size is also 44 µm, with 99% purity. The grain size of manganese with a purity of 99.3% was 44 µm. The last element is nickel with a grain size of 44 µm and a purity of 99%. Individual powdered metals were carefully stored in special containers. They were not exposed to unnecessary external atmospheric influences.

Alloys were prepared by arc melting the metals mentioned at the Institute of Materials Research of the Slovak Academy of Sciences in Košice, where there is a fully built and operational Laboratory of Advanced Alloys. Prior to the production of alloys the loss of mass due to evaporation of individual elements in the melting process was determined. The volatility of elements was taken into consideration when creating specific alloys. Melting of batches took place in an inert atmosphere of argon of 99.999% purity. Each alloy was re-smelted at least 3 times for the best possible chemical homogeneity in the volume of the cast.

### 2.1 Preparation of allows

#### 2.1.1 Alloy Ti-Cr-Mn

The total mass of the alloy Ti-Cr-Mn is 82.7 g, which represents a volume of 13 ml. Figure 2 illustrates the alloy Ti-Cr-Mn in granular form before and after the measurement. By comparing the samples before and after the measurement, we concluded that the partial alloy absorbing hydrogen in the hydrogen and deflation, there was some cleavage of the granules. Therefore the alloy crushed – in the cluster rolling mills as fine fraction. The milled alloy Ti-Cr-Mn (fig. 3) was subjected to measurements under the same conditions as the granulated.

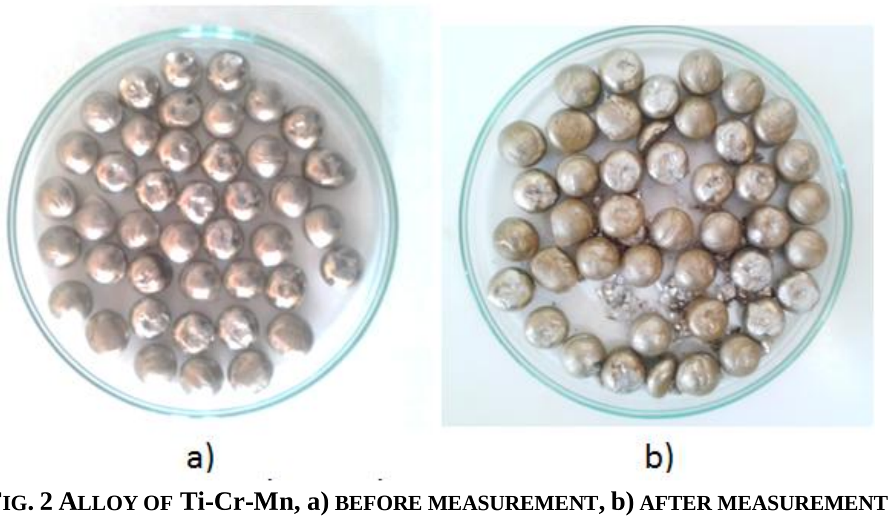



FIG. 2 ALLOY OF Ti-Cr-Mn, a) BEFORE MEASUREMENT, b) AFTER MEASUREMENT

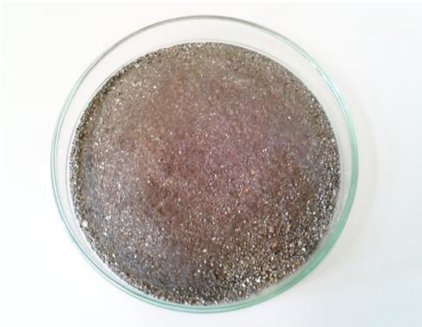


**FIG. 3 GROUND ALLOY Ti-Cr-Mn**

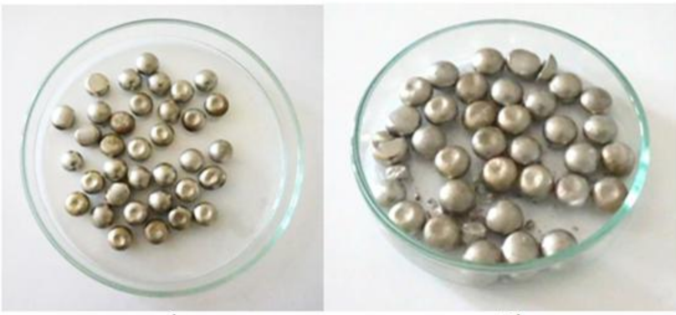
### 2.1.2 Alloy Ti-Cr-Ni

Alloy Ti-Cr-Ni with an overall mass is 69.6 g, which represents a volume of 10.8 ml.

**FIG. 4 ALLOY Ti-Cr-Ni**

### 2.1.3 Alloy on a base of Ti-Cr-$Ni_{0.5}$-$Mn_{0.5}$

Alloy Ti-Cr-$Ni_{0,5}$-$Mn_{0,5}$ weighs 68.3 g, representing a volume of 10.7 ml.



a) b)

**FIG. 5 ALLOY OF Ti-Cr-$Ni_{0,5}$-$Mn_{0,5}$, a) BEFORE MEASUREMENT, b) AFTER MEASUREMENT**

## III. MEASURING STORAGE CAPACITY OF ABSORPTION MATERIALS

Measurement is essential to research the storage capacity of selected types of metal hydride respecting the operating pressure for the predefined acceptable operating temperatures.

At present it is already possible to determine the absorption properties of any sample using a thermo gravimetric sorption analyser, which can determine the mass of the storage other than the percentage of the amount of surface area, porosity of the material, selectivity, and other various gases. The experiment chose the volumetric method, in which tracks the bulk amount of hydrogen discharged from the tank and the pressure of hydrogen in the tank. The quantity of stored hydrogen is then determined indirectly.

As with some types of metal hydride, degradation of storage capacity occurs, when the absorption properties are measured, therefore, work is done with higher purity hydrogen (99.999%). First, the alloys Ti-Cr-Ni, Cr-Ti-$Ni_{0.5}$ $Mn_{0.5}$ and Ti-Cr-Mn in granular form were subjected to experimental measurements.

On fig. 6 we can see the measuring apparatus connected to the absorption tank. To measure the absorption properties of alloys under isothermal conditions in a temperature range of -40 ° C to + 20 ° C, the temperature should be kept constant including in the case of the generation of heat during the absorption.

**FIG. 6 MEASURING STAND FOR DETERMINING THE STORAGE CAPACITY OF SELECTED METAL HYDRIDE ALLOYS**

To maintain constant temperatures (-40 °C, -30 °C, -20 °C and 0 °C) a liquid-nitrogen based cooler was used. To maintain higher temperatures (+ 10 ° C and + 20 ° C) in the storage container a heat sink on the basis of Peltier elements was used. Before the measurement of the absorption properties, it is necessary to fill the container with the alloy whose storage characteristics are to be determined. The measurement procedure is as follows:

- Vacuuming the system using pumps
- Opening the pressure vessel with the reducing valve, which contains hydrogen with a purity of 99.999% at a pressure of 20 MPa.
- Opening the inlet valves - start filling the absorption reservoir of hydrogen at 82 bar pressure
- Releasing hydrogen from the container, followed by sequential measurement of the volume of the hydrogen and pressure in the vessel.

The quantity of hydrogen is determined by the volumetric method. At the same time the relative pressure in the storage facility, temperature and pressure in the measuring cylinder are recorded.

### 3.1 Measuring the storage capacity of MH alloys under isothermic conditions

In the following graphs (Fig. 7 to 10) it is possible to see the dependence of mass storage percent of different alloys on the pressure in the storage vessel for various temperatures.

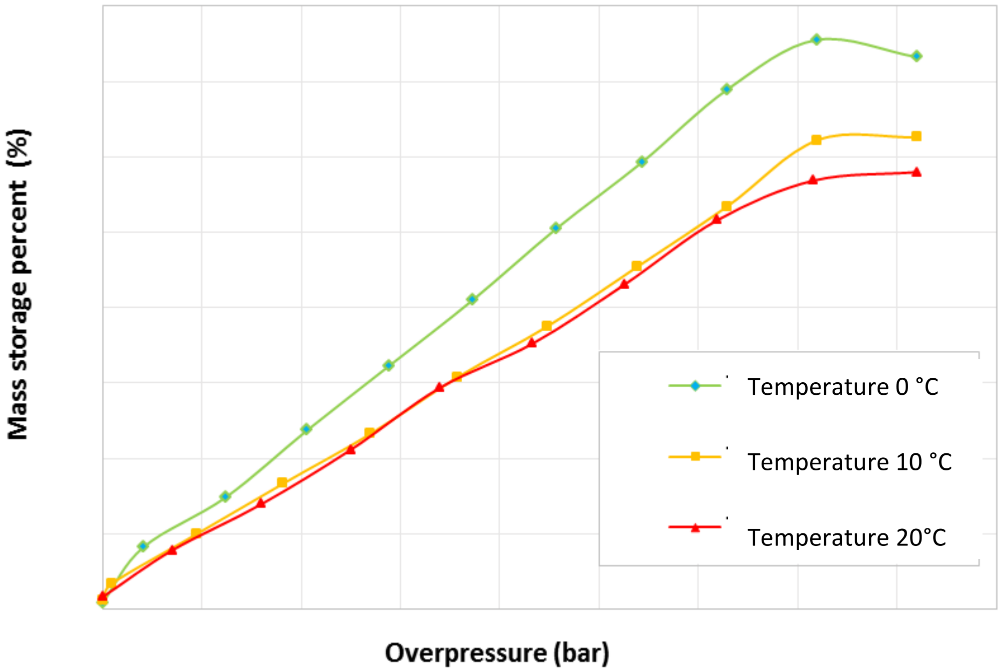



**FIG. 7 DEPENDENCE OF MASS STORAGE PERCENT OF GRANULATED ALLOY *Ti-Cr-Mn* ON OVERPRESSURE FOR DIFFERENT TEMPERATURES**

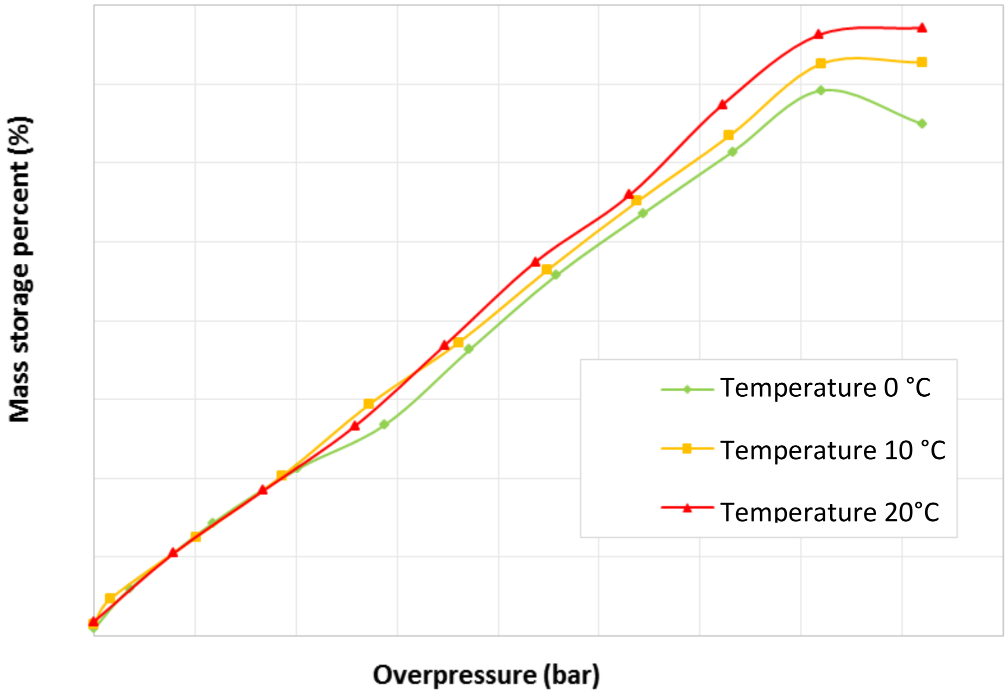



**FIG. 8 DEPENDENCE OF MASS STORAGE PERCENT OF GRANULATED ALLOY Ti-Cr-Ni ON OVERPRESSURE FOR DIFFERENT TEMPERATURES**
**(green 0 °C yellow 10 °C red 20 °C)**

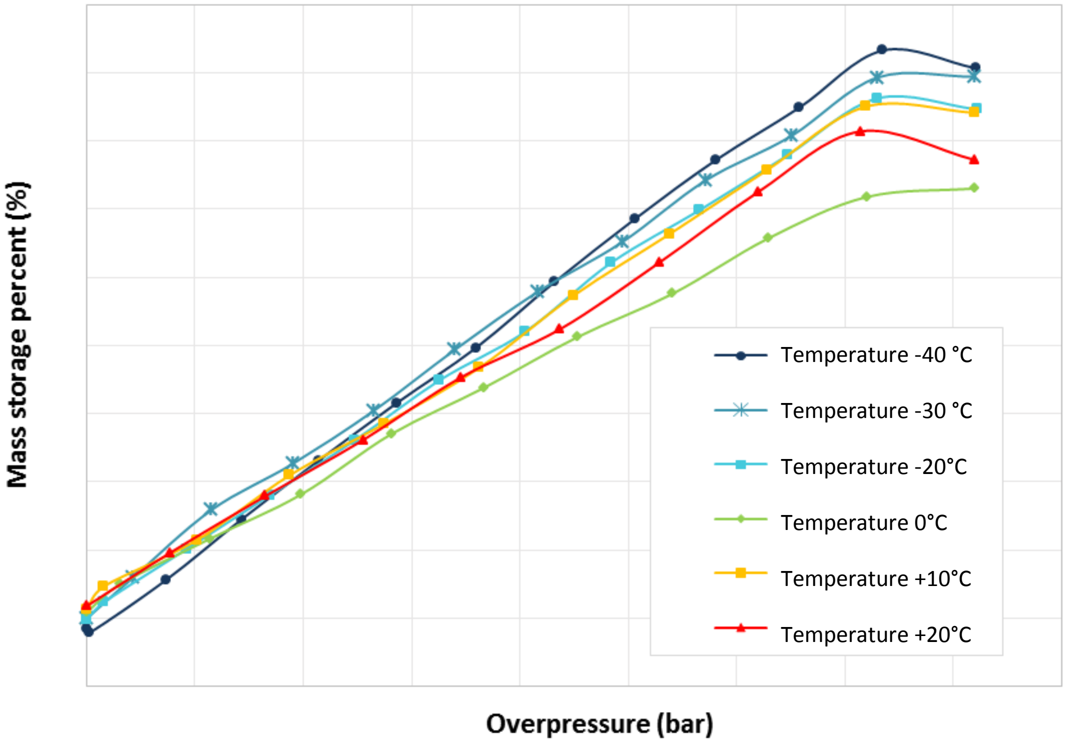



**FIG. 9 DEPENDENCE OF MASS STORAGE PERCENT OF GRANULATED ALLOY Ti-Cr-Ni-Mn ON OVERPRESSURE FOR DIFFERENT TEMPERATURES**

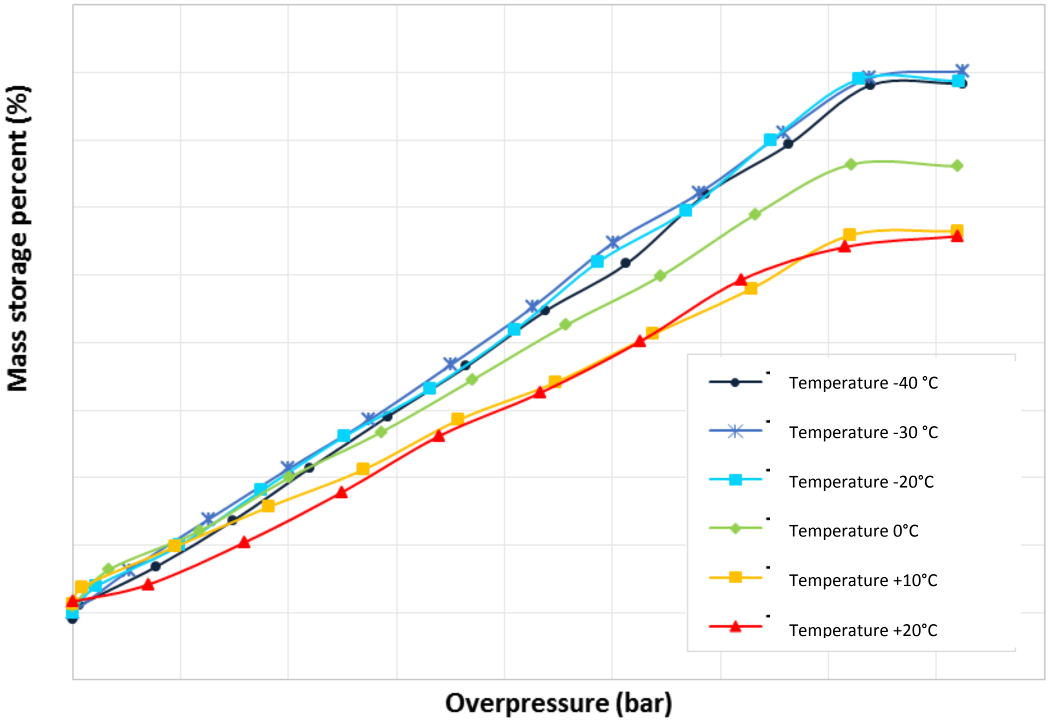



**FIG. 10 DEPENDENCE OF MASS STORAGE PERCENT OF GRANULATED ALLOY Ti-Cr-$Ni_{0,5}$-$Mn_{0,5}$ ON OVERPRESSURE FOR DIFFERENT TEMPERATURES**

The highest values of the mass storage percent (almost 0.17 by wt.%) was achieved by the alloy Ti-Cr-Mn-Ni at -40 °C.

However the use of any alloy tested by us at temperatures of from -40 ° C to 20 ° C and pressures of from 5 bar to 82 bar is ineffective. This follows from the graphical dependence of mass of stored hydrogen on the pressure in the container using a variety of absorbents at all temperatures.

An important parameter is not just the mere composition of the alloy but also its structure, which will be the next subject of research. With arc melting followed by rapid cooling it is likely to form as an amorphous structure, while the additional recrystallization of reduction of surface-bound oxygen in a hydrogen atmosphere should significantly increase storage capacity.

## IV. CONCLUSION

Hydrogen storage is a key problem for implementing hydrogen technology and the economic use of the element. The familiar approaches of pressure and cryogenic storage do not offer the desired safety and their implementation will require significant amounts of energy. The transition to metal hydride storage opens new opportunities for safer storage, while facing with the problem of compliance with the minimum mass of the hydrogen storage for optimal use. Their storage capacity is rarely achieved by the required storage capacity of 6.5 % by mass and therefore research is being conducted into processing known and searching for new alloys. The aim is to achieve the greatest storage capacity while maintaining an acceptable price with the highest cyclic stability of the hydride. The biggest expectations are primarily from automobile manufacturers, who are limited mainly by storage of hydrogen, leading to limited range of cars.

## ACKNOWLEDGEMENTS

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