Characterisation of powder and pellets

In this deliverable the characterisations of powder and pellets produced for the HyCARE system and performed by the partners are discussed.

GKN produced at the industrial scale up to 200 kg as a first batch for the prototype tank and afterwards up to 4 tons for the final demonstration tank the powder material of the selected composition.
The produced material that includes 2% of binder (**Lot IX-20015, 200 kg**) has been distributed among the **partners** in form of powder and pellets for its characterization and the development of a first prototype module of the integrated system. Furthermore, the large 4 t production has been characterized at **GKN** (**Lot 570119000/1-4, 4 tons**) and related results are also presented.

In details: structure, microstructure, particle size, density, thermal conductivity, heat capacity, composition, hydrogen storage properties (reversible capacity, thermodynamics, kinetics), poisoning and cycling properties have been reported.

*Samples and synthesis (**GKN**)*

The large volume of 4 t of powder for the demonstrator (**Lot 570119000/1-4, 4 t**) was manufacture. **Figure 1** shows 4 big-bags with 1 t of powder each.

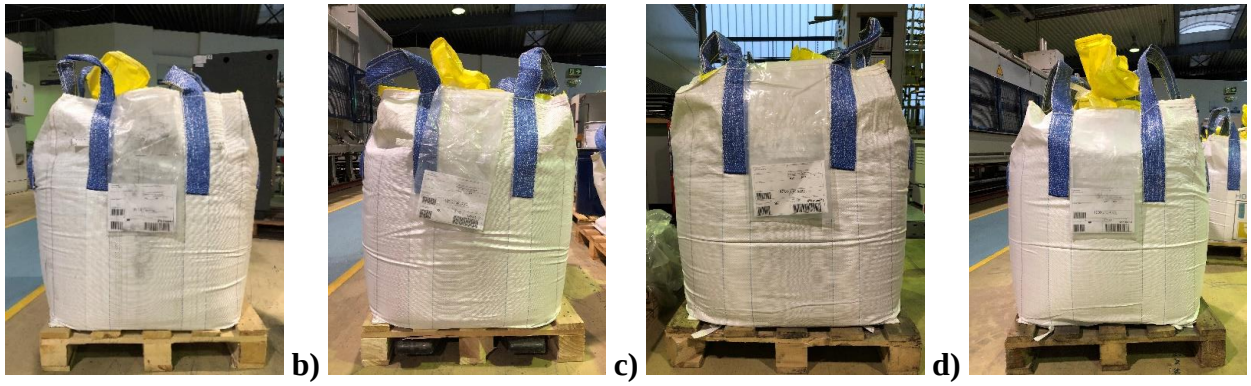

Figure 1 – Pictures of the 4 Lot bags containing 1 t of produced powder: **a)** Lot 570119000/1, **b)** Lot 570119000/2, **c)** Lot 570119000/3 and **d)** Lot 570119000/4.

Characterizations

Chemical analysis and oxygen content

Chemical analysis of the powder sample (**Lot IX-20015**) by ICP-OES at **CNRS** confirmed the selected nominal composition.
Some oxygen, thus oxide phase is present in the produced material. After activation and cycling, the oxygen content increased. A possible motivation for this can be found in the increase of surface area and the formation of new oxide layers, despite the low oxygen concentration in the Ar-atmosphere of the glovebox; this suggest that the activated material is very reactive.

Microstructural and structural characterization

The particles form was investigated by **GKN** by SEM analysis. **Figure 2** shows the particle form of powder **Lot 570119000-1** exemplarily. The typical structure of brittle crushed powder with trans-crystalline fractures is clearly observed.

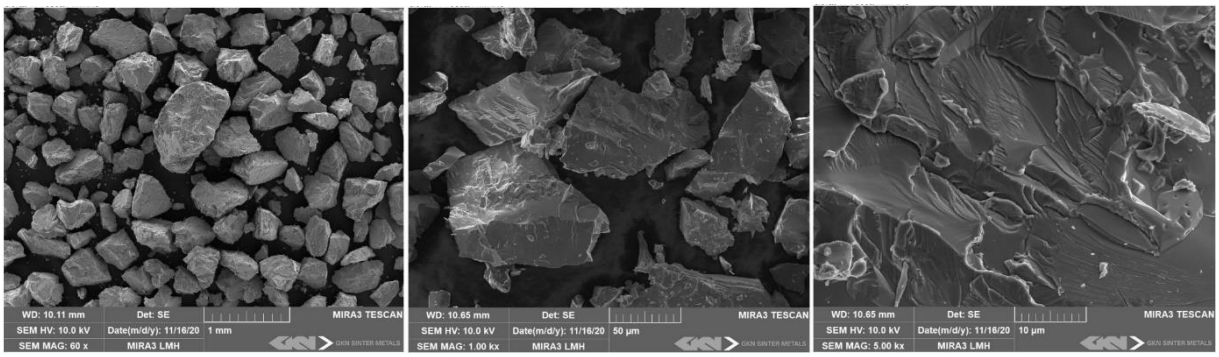

Figure 2 – Crushed particles analysed at **GKN** by SEM (**Lot 570119000-1**).

At **CNRS** and **UNITO**, the pellets from **Lot IX-20015** were crushed, the loose powder was embedded in a resin, polished and analysed by EPMA and SEM respectively.

Considering the SEM elemental maps performed at **UNITO** for the GKN pellet, shows that Mn is quite homogenously distributed, Ti and Fe are also homogenously distributed in the matrix, and furthermore a Ti-rich phase with lower amount of Fe can be identified.

This result, together with the other EDX analysis performed (**Figure 3**), confirms the presence of a Ti-rich phase with $Ti_{80}(FeMn)_{20}$ composition, plus a possible oxide Ti_4Fe_2O-type phase and the FeTi matrix, as it will be confirmed from the XRD analysis.

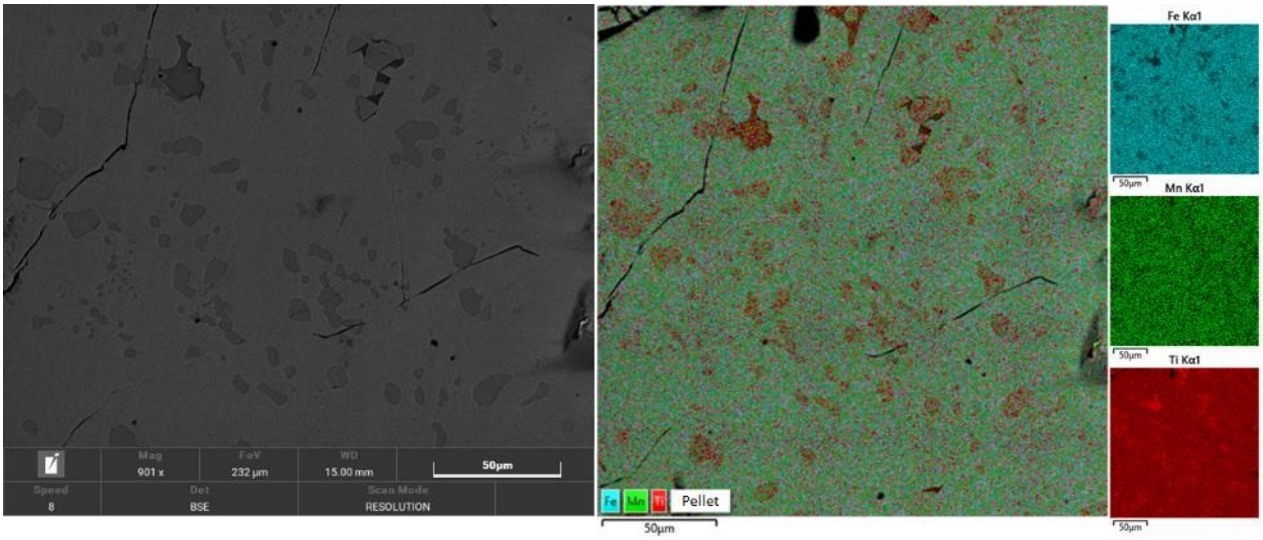

Figure 3 – EDX mapping analysis performed at **UNITO** by SEM on the pellet (**Lot IX-20015**).

Phase lattice parameters and phase abundance have been determined by Rietveld refinement of XRD patterns by **UNITO** (**Figure 4**) as well, which are in good agreement with that determine by **CNRS**. Results evidence approx. 11-13 wt% of oxide and 1-2 wt.% of β-Ti. FeTi adopt a cubic CsCl-type structure, space group *Pm-3m*, with cell parameter that variates between 2.981-2.985 Å as determined by **UNITO** and **CNRS**.

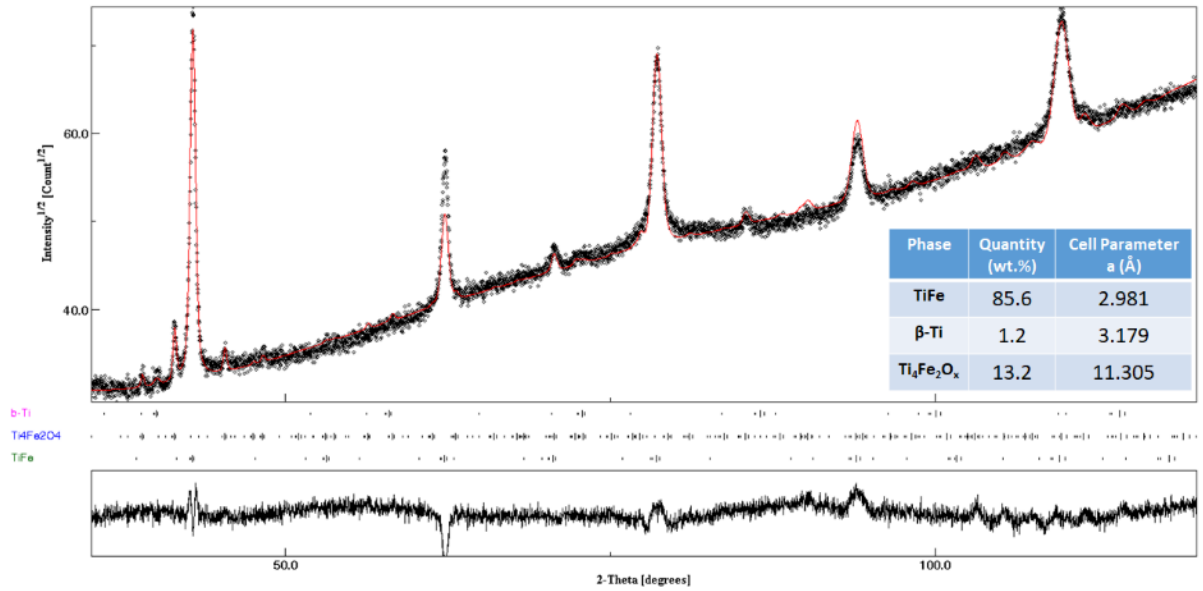

Figure 4 – XRD patterns and Rietveld Refinements (**Lot IX-20015**) performed by **UNITO** in capillary geometry.

Particle size, density determinations, thermal conductivity and heat capacities

Particle size distribution determined by sieve analysis and laser diffraction have been determined by **GKN**.

From the analysis performed at **HZG** on **Lot IX-20015**, it can be noticed that the as received sample has a quite homogeneous particle size distribution, then with the activation process and subsequent cycling, the particle size was reduced considerably.

The values for density have been determined to be in a close range; a difference can be noticed between the as received and activated samples, the latter having a slightly lower value for apparent density.
This effect can be explained with the change in the distribution of particle size after the first reaction with hydrogen has occurred; bigger particles decrepitate into smaller ones and the porosity increases.
The density for the pellet (**Lot IX-20015**) resulted 4.85 g/cm^3.

The results of the heat capacity measures by **HZG** have been reported, and it can be noticed that, also in this case, the difference between batches and treatments is not so significant. However, the effect of the reduced density after activation observed before influences the heat capacity, due to the larger amount of voids between particles of the powder. A further validation of this hypothesis comes from the comparison considering the values per unit of mass and those per unit of volume: while the former are almost unaffected by the activation treatment, especially in the case of the industrial batch, the latter display a more significant discrepancy. In general, the specific heat capacity values are well aligned with those of iron and titanium, main components of the alloy (i.e. 0.412 and 0.523 J/gK, respectively).
The properties of the pelletized material confirm and reinforce the idea: the capacity per unit mass does not change drastically, but it is possible to notice a marked increase in the capacity per unit of volume, due to the increased density and the presence of the binder to replace most of the porosity.
The reduced porosity and the binder are also the reason for an improved thermal conductivity.

Hydrogenation properties

Activation behaviour and storage capacity

The pellet (**Lot IX-20015**) was successfully activated.

A good capacity and kinetic was reached after the first hydrogenation and 4 further cycles. The total capacity results to be as high as 1.72 wt.%.

Thermodynamics

PCI curves and thermodynamics for the pellet (**Lot IX-20015**) have been determined by **CNRS** at different temperatures.
The PCI curves present slopped plateaus as already evidenced in previous GKN industrially produced samples. As already discussed in previous reports, the slope is attributed to the chemical inhomogeneity of the sample.
The reversible capacity of the samples between 2 and 25 bar at 55 °C is 1.2 wt.%, slightly lower than the initial target of HyCARE (1.3 wt.%).
Determined thermodynamics have been reported in detail with an average absorption enthalpy and entropy of -29.6 kJ/mol and -131 J/molK, respectively, and an average desorption enthalpy and entropy of 30.2 kJ/mol and 128 J/molK, respectively.

Kinetics

At **HZG**, to assess the kinetic properties of **Lot IX-20015**, measures were performed at a constant temperature of 55 °C and five different absorption pressures (25, 20, 15, 10, and 5 bar) and three different desorption pressures (4, 2, and 1 bar) were used in the first round of tests, resulting in 15 cycles; a short evacuation, included in the procedure to flush the atmosphere inside the sample holder between cycles, ensured the comparability of the starting condition of the sample.

The results of the kinetics measurements show that, in the majority of the temperature and pressure settings examined, the reaction is completed in less than 10 minutes, or at least the technically relevant fraction of it takes place in this short time range. The difference in the amounts of hydrogen exchanged at different pressures is in good agreement with the data coming from the isotherms, showing the influence of the slope of the plateaus on the final quantities absorbed and desorbed. These are affected prominently, while the kinetics are almost unaffected by the pressure; the last fraction of all the curves in the graphs is practically flat, suggesting that the reaction cannot proceed further due to thermodynamic constraints and not to hindered kinetics.
Concerning the final quantity of hydrogen reached that is lower than the gravimetric capacity predicted by the isotherms, a technical explanation helps understanding this phenomenon. There is a tiny time interval between the opening of the two valves to the sample and reference volume and the actual differential pressure measurements, set to avoid the fluctuations due to the hydrogen flowing into the mentioned volumes. The reaction is so fast that in this time interval, it has already started exchanging an amount hydrogen, which is not detected. For this reason, measurements performed in quasi-equilibrium conditions are more reliable to assess the gravimetric capacity.
The final quantities of hydrogen reached during absorption are not influenced by the desorption pressure used in the set of tests, while the released quantities are influenced both by the settings used during desorption itself, and the pressure used to previously load the sample. The results range quite regularly between the most convenient setting (releasing from 25 to 1 bar) and the most penalized one (from 5 to 4 bar), where almost no reaction is detected.

Preliminary testing in order to evaluate the interaction between metal hydride pellet and inner heating and cooling pipes during cycling

The pellet geometry of three experiment setups varied that way that the diameter of the compacts was increased step by step, reducing radial growth. In parallel the height of the axial spaces (rings) was increased with the aim to compensate limited radial growth by allowing axial growth.
During testing, it was clearly observed that the pellet in the 1st setup shows material break off after testing, while only cracks are observed in pellet in the 2nd setup, and pellet has no cracks in the 3rd setup.

As result of the preliminary testing it can be concluded that not provided radial growth of the pellets can be compensated by axial growth. With respect to heat transfer the 3rd experimental setup is the most promising. However, the allowed linear radial growth of the pellet was reduced to 3.4 % which is very low. Inacceptable high stress on the tank wall during pellet expansion cannot be excluded. Due to the double wall tank design of the available test tank, stresses on the tank wall cannot be measured during the experiment.
For the prototype the pellet dimensions were chosen according to the 2nd experimental setup with the aim to keep the mechanical pressure on the tank wall in an acceptable range and to prevent material break offs of the pellets during cycling.

Conclusions

Testing, among HyCARE partners, of materials produced and processed by GKN at the large scale has been conducted and reported.

The following objective has been achieved and established:

- 200 kg of powder (**Lot.IX-20015**) for the first prototype module and the total amount of powder needed for the integrated system (4 tons, **Lot.570119000**) have been successfully produced.
- Chemical analyses of the sample produced at large scale evidence a nominal composition that matches the target. Lower amount of **oxygen** is detected in **Lot.570119000**. Oxygen content increased on **Lot.IX-20015** after activation due to an increase of surface area and the formation of new oxide layers (highly reactive activated powder).
- Microstructural and compositional analysis performed by microscopy show a main **Ti(Fe,Mn)** phase, a secondary phase that corresponds to the oxide phase, i.e. **$(Ti,Mn)_4Fe_2O_x$**, and a **β-$Ti_{80}(Fe,Mn)_{20}$** as a third phase.
- XRD analysis confirmed the presence of approx. **11-13 wt% of oxide** and **1-2 wt.% of β-Ti phase**. **FeTi** main phase has a cell parameter that variates between **2.981-2.985 Å**.
- Particle size distribution, densities and thermal conductivities have been determined.
- The materials have been easily activated by the optimised procedure previously developed.
- PCI curves and **thermodynamics** have been determined for **Lot IX-20015**, evidencing **sloping plateau** and a **reversible capacity** of the samples between 2 and 25 bar at 55 °C equal to **1.2 wt.%**. **Average absorption enthalpy** and **entropy** are equal to **-29.6 kJ/mol** and **-131 J/molK**, respectively, and the **average desorption enthalpy** and **entropy** are **30.2 kJ/mol** and **128 J/molK**, respectively.
- Absorption and desorption reactions are completed in **less than 10 minutes** (good kinetics).
- Preliminary test to evaluate the interaction between metal hydride pellet and inner heating and cooling pipes during cycling have been performed. For the **prototype** the **pellet** dimensions were chosen according to the **2nd experimental setup** with the aim to keep the mechanical pressure on the tank wall in an acceptable range and to prevent material break offs of the pellets during cycling.