Selected alloy characterisation

For this deliverable, results of **characterisation on the selected alloy** for the project has been discussed. Considering the goals of the project, an overview on the alloy structure, microstructure, reversible capacity, hydrogen storage properties, thermodynamics, kinetics, activation and cycling properties is reported.

SEM analysis (**Figure 1**) clearly evidenced the presence of a low amount of precipitates as secondary phases. The matrix can be assigned to the FeTi-type intermetallic compound. Because of alloy off-stoichiometry with respect to the 1:1 Ti-Fe composition, also β-$Ti_{80}Fe_{20}$ solid solution phase can be observed, in accordance with the Fe-Mn-Ti ternary phase diagram. A second phase with Ti:Fe ratio of 2:1 is detected as well, which can be assigned to the Ti_4Fe_2O-type phase. However, from EMPA analysis it was not possible to detect and determine the oxygen amount. Mn is homogenously distributed in all particles and phases, and the composition of the alloy is homogeneous over the sample thanks to the annealing process.

XRD analysis and Rietveld refinement confirm the presence of a low amount of β-$Ti_{80}Fe_{20}$ solid solution and Ti_4Fe_2O secondary phases.

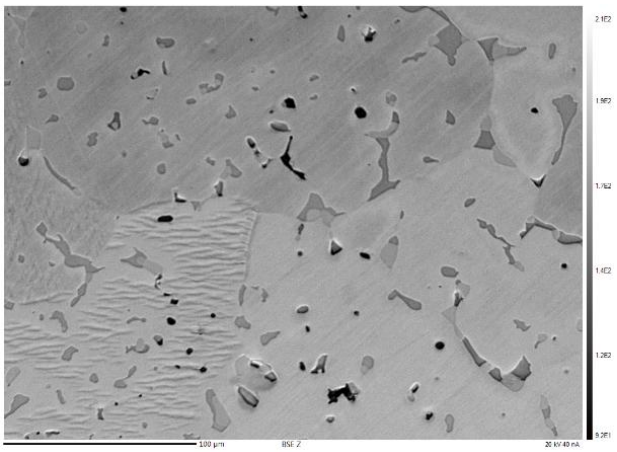

Figure 1 – SEM images of selected alloy for the HyCARE project.

The alloy was easily **activated** at room temperature (RT) under 25 bar of H_2. The presence of small amount of secondary, phases such as β-$Ti_{80}Fe_{20}$ solid solution and Ti_4Fe_2O, plays a role and helps the activation process.[1] It was reported that they facilitate hydrogen penetration across the alloy surface and subsequent first hydrogen absorption in alloy bulk.[1] The material absorbs hydrogen at RT and under 25 bar after 7 hours of incubation time. After the first absorption, which displays slow **kinetics** (**Figure 2, A**), the sample was cycled 5 times, till stable and fast hydrogenation kinetics was reached. After activation, the hydrogen uptake and release display very fast kinetics with t_{90} ~ 1.5 minutes (**Figure 2, B**). t_{90} represents the time required to reach 90% of the hydrogenation or dehydrogenation reaction, compared to the final hydrogen content at infinite time (equilibrium).

According to the HyCARE goals, the **thermodynamic window**, in which the hydrogen storage properties of the active material should be investigated, has been defined within the range $2 \leq P_{H2} \leq 20$ bar and $25 \leq T \leq 55$ °C. For this reason, the reversible capacity has been determined from **PCI curves** between 2 and 20 bar H_2 at fixed temperatures. The hysteresis between absorption and desorption isotherms is not too much extended, and it guarantees high reversible capacities. The material, especially at 55 °C, presents a quite flat PCI curve with high reversible capacity (1.42 wt%) in the defined thermodynamic window. The thermodynamics of hydrogen sorption reactions (ΔH, enthalpy and ΔS, entropy,) has be determined measuring PCI at different temperatures by the Van't Hoff equation: $\ln P_{H_2}^{eq} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$, R is the gas constant.

Since the sample presents high reversible capacity at 55 °C, cycling tests in absorption under 20 bar H_2 and desorption at 2 bar H_2 have been performed. A slight drop in reversible capacity is detected upon **cycling** (**Figure 3**), that is approaching to a steady state after 100 cycles. It presents a 0.26 wt% loss after 250 cycles, which represents an average capacity decay of 0.001 wt.% per cycle, much lower (i.e. much better) that the target of the project (0.002 wt.% per cycle). Upon cycling, the reversible capacity decreases. However, comparing the PCI curves of fresh sample and the PCI curves after 100 and 250 cycles, this capacity degradation equally affects both first and second plateau. It decreases the total reversible capacity compared

to the freshly activated sample. The PCI after 250 cycles is similar to the one obtained after 100 cycles, confirming the small degradation of the sample hydrogen storage properties after the initial cycling.

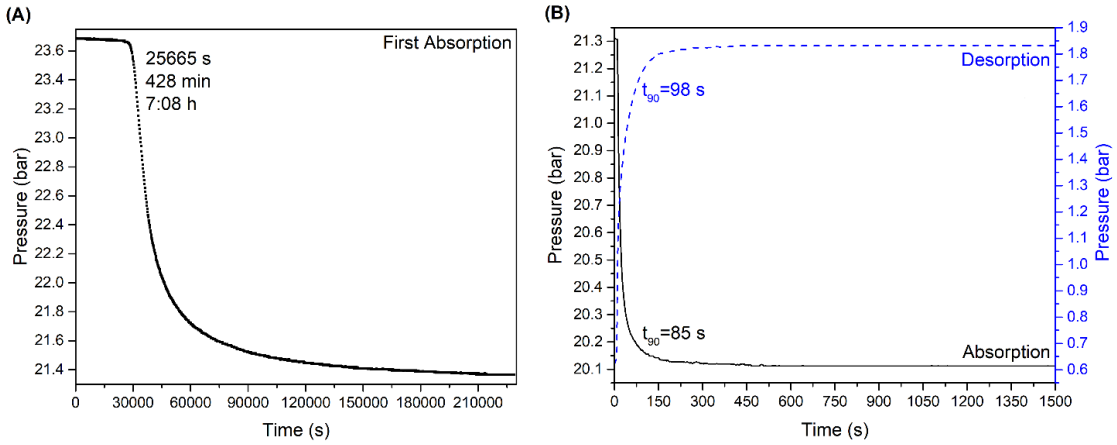

Figure 2 – Pressure vs time for selected alloy, representative of its kinetics during the first absorption (A) and after activation (B).

In conclusion, the alloy selected for the HyCARE project has been synthetized and characterized at the lab-scale. It presents chemical homogeneity and quite flat PCI curves, thanks to the annealing treatment after alloy synthesis. It is characterised by a major FeTi matrix and minor contents of β-$Ti_{80}Fe_{20}$ solid solution and Ti_4Fe_2O oxide precipitate phases. The presence of small amount of Mn in the intermetallic compound, β-$Ti_{80}Fe_{20}$ solid solution and Ti_4Fe_2O oxide secondary phases is crucial for improving the activation procedure. In fact, the material was easily activated at RT and under 25 bar of H_2 after 7 hours of incubation time. It has a high initial reversible capacity at 55 °C (1.42 wt%) and good cyclability (capacity decay of 0.001 wt.% per cycle). The thermal treatment guarantees the chemical homogeneity of the samples and almost flat pressure plateaus, which improve the reversible capacity of the alloys. The kinetics and thermodynamics of the alloy have been determined, and they satisfy the targets of the HyCARE project.

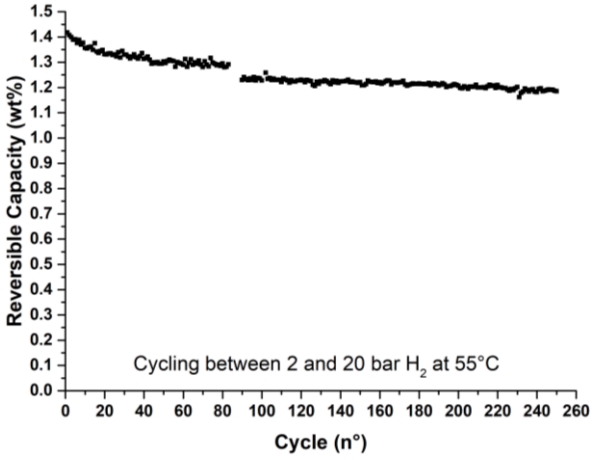

Figure 3 – Reversible capacity of the sample, between 20 and 2 bar H_2 at 55°C as a function of absorption-desorption cycles.

References

1. Rupp, B. On the Charge in Physical Properties of $Ti_{4-x}Fe_{2+x}O_y$ during Idrogenation. I: Activation Behaviour of Ternary Oxydes $Ti_{4-x}Fe_{2+x}O_y$ and β-Ti. *J. less Common Met.* **1984**, *104*, 51–63.