Underlying causes of the improved storage capacity of $TiMn_{1.5}$ by annealing treatment

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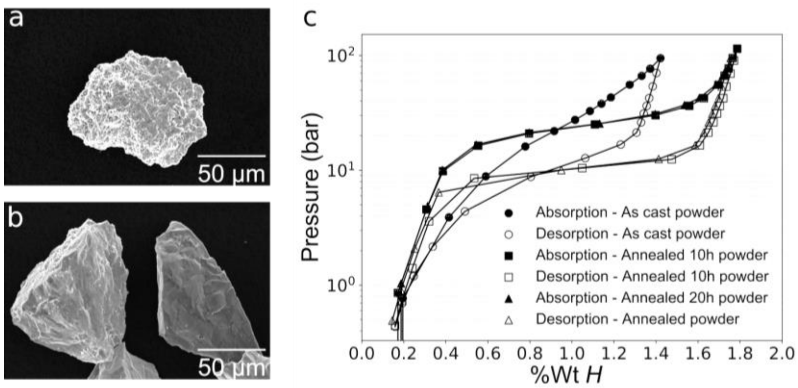
Hydrogen storage in solid form by reversible hydriding of intermetallic compounds is a relevant technology for stationary applications or heavy mobility. The move towards low-carbon hydrogen-energy requires that the used compounds are highly efficient (gravimetric and volumetric capacity), sober (operating T and P close to ambient), easy to source and process, and regenerable or recyclable.

Ti-Mn-based alloys that can be directly activated in ground powder form are high potential candidates. The H-sorption properties of Ti-Mn-based alloys powders have been studied since the 1980's [1-3]. Gamo *et al* state in [1] that $TiMn_{1.5}$ is the most suitable formulation and that an annealing treatment at 1100°C for 20h increases the reversible H2 storage, inducing saturation to over 0.9 H/M for a residual amount of trapped H lowered to 0.1 H/M. It also flattens the plateau on the PCI curves. However, the metallurgical mechanisms leading to this improvement have not been clearly elucidated. Later, the correlation between the microstructural characteristics, the component substitution and the H-sorption for TiMn-based alloys have been studied [4-6]. Hereafter, the annealing-induced microstructure and its correlation with improved storage properties are investigated.



The amount of porous, friable particles (a) among the faceted particles (b) is 20% higher. Extension and flattening of the PCI curves (c)

$TiMn_{1.5}$ powder obtained by induction furnace, casting followed by crushing is synthetized. We show that annealing under argon flush at 1100°C for 10h or 20h has the same effect on H-sorption. We have studied the changes induced at the particle, microstructure and crystal lattice scales, using various observation and characterization methods: optical microscopy and SEM, EDS assay, X-ray diffractometry, Sievert's apparatus. SEM images show that some of the faceted particles are transformed in crumbly, porous ones. Their number increases by 20% after annealing. Mapping analysis by EDS shows domains of $TiMn_{\alpha}$ embedded in a more Mn-rich matrix. The matrix contains 60% Mn and 40% Ti, suggesting a Laves phase C14 (from $TiMn_{1.5}$ to $TiMn_2$). DRX confirms, in both raw and treated samples, a Laves C14 structure, some TiMnα and a small amount of Ti08Mn92 (could be Mnα). After treatment, TiMnα decreases and $Ti_{08}Mn_{92}$ increases. Rietveld refinement indicates a significant relaxation of residual stress, especially in the C14 phase. It tends to suggest that the improvement in storage potential is caused by the synergy of these modifications at different scales.

References

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