

SEM analysis of the Mg-MgH₂ phase transformation.

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MgH₂ is considered a priority material for the solid-state H₂ storage due to the high hydrogen capacity and to its reversibility in the desorption/absorption cycling. However, the technological application still experience several problems mainly related to the thermodynamic stability toward decomposition so that hydrogen is often released at temperatures too high for many applications, and to the slow rates of H₂ release and uptake, related to kinetic constraints in the Mg-MgH₂ phase transformation. In the last years, many research efforts had the purpose of reduce the decomposition temperature and to fasten the sorption reaction. Up to now, the addition of catalyst particles and nanostructuring by high energy ball-milling are at the basis of the strongest improvements, giving rise to materials with strongly enhanced reaction kinetics.

For a better understanding of the mechanisms of reaction, we propose to integrate the traditional kinetics analysis, based on the analysis of the reaction rate during isothermal phase transformations, with a metallographic approach able to provide information on the microstructure of partially transformed sample.

To this purpose we have developed a method based on low voltage SEM observation of cross sectional samples made of partially transformed material, so that they are constituted by a mixture of Mg and MgH₂. The spatial distribution of the two phases can in fact provide important issues in the phase transformation which are difficult to assess by indirect methods, like nucleation site, nucleation rate and so on. The method is based on the different SE yield displayed by the insulating MgH₂ and by the metallic Mg in a low voltage SEM observation [1]. In fact, despite the multiplicity of effect which can affect the contrast in the observation of metal-insulator compound, in the present case, where the samples are constituted by a fine distribution of one phase into the other, the main contrast features can be easily interpreted on the basis expected emission behaviour. In fact, at low voltage the emissivity of the insulator is limited to the unity by surface charging effects, while a metal has generally a larger secondary electron yields [2].

In order to exploit this kind of contrast in a practical situation where the internal microstructure of a powder sample has to be studied, the sample preparation method is of primary importance. In order to provide to the powder particles a matrix necessary for the polishing and a ground contact necessary for dispersing the impinging current, the powders have been embedded in a conductive matrix by a mechanical method already described [3].

Three kind of materials have been studied, in order to understand the role of the catalyst and of defects in the MgH₂ ↔ Mg + H₂ reaction: as received MgH₂, 10h milled MgH₂ and 10h milled MgH₂ with 5wt% of Fe dispersed within, acting as reaction accelerator. The samples have been subjected to partial phase transformation in both directions so that they are constituted by a dispersion of about 10% of the product phase in the parent matrix.

Experimental results are reported Figure 1 where typical sample cross sections observed at 1 kV of beam primary energy are reported. The clear contrast occurring between Mg (light grey) and MgH₂ (dark grey) allows distinguishing the details of the microstructure, and in

particular the distribution of the growing phases. The lighter particles in Figure 1c-f are assigned to the Fe particles finely dispersed in the Mg or MgH₂ phase.

The metallographic analysis easily shows the differences in the two reactions. In fact the decomposition of pure MgH₂ proceeds through Mg nucleation at the sample surface. When catalyst particles are added nucleation occurs also at this kind of impurities so that nucleation through the whole sample is observed. On the contrary when Mg transforms to MgH₂, the surface does not appear to have any particular role and the nucleation occurs at structural defects. A higher defect density in ball milled sample reflects in a higher nuclei density and the catalyst particle appear, in this case, to behave like structural defects..

This kind of information, coupled with the classical kinetic analysis allow a better understanding of the details of the phase transformation which can be so described even beyond the definition of the reaction rate limiting step.

1. M. Vittori Antisari et al., *Intermetallics* (2009) *in press*.
2. J. Cazaux, *Scanning* 26 (2004), p. 181-203
3. A. Montone, M. Vittori Antisari, *Micron* 34 (2003), p. 79–83
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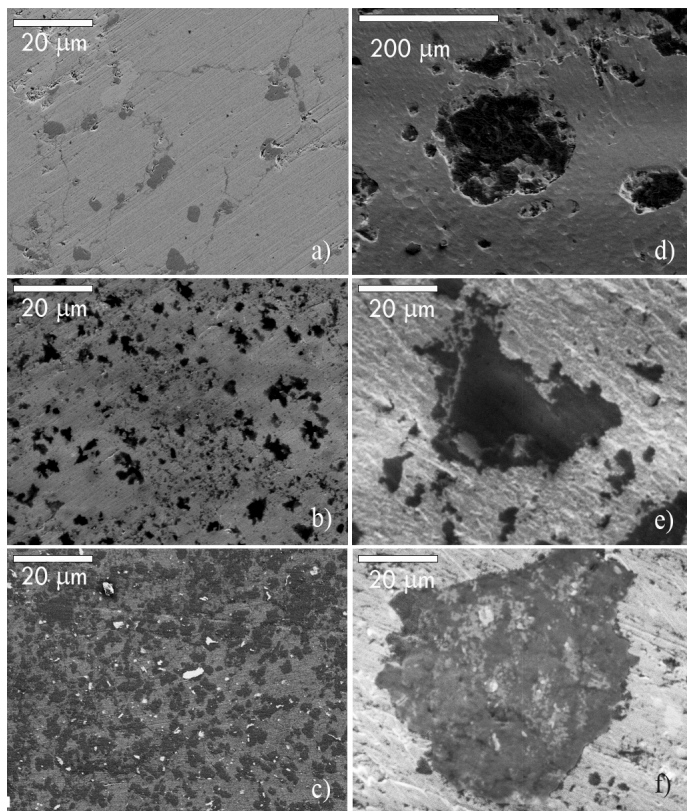


Figure 1. SE images at 1kV at different magnification of a) unmilled MgH₂, b) 10h milled MgH₂ and c) 10h milled MgH₂ catalyzed with Fe 5wt.% partially absorbed and of d) unmilled MgH₂, e) 10h milled MgH₂ and f) 10h milled MgH₂ catalyzed with Fe 5wt.% partially desorbed. Lighter area surrounding the particles in d, e and f is aluminum matrix.