

## MICROSTRUCTURAL CHARACTERIZATION OF NANOSTRUCTURED COMPOUNDS ON HYDRIDE SYSTEMS BY MEANS OF TRANSMISSION ELECTRON MICROSCOPY

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One of the main limitations for the implementation of hydrogen as energy carrier is the lack of an efficient and safe hydrogen storage system. Hydrogen storage in solid state through the formation of hydride compounds is a potential alternative to address this problem [1]. There are several metals and compounds which react with hydrogen to form hydrides. Among them, magnesium hydride ( $MgH_2$ ) and its combinations with complex hydrides such as lithium borohydride ( $LiBH_4$ ) present potential characteristics for being used as hydrogen storage medium for practical applications.  $MgH_2$  combines a relatively large hydrogen capacity of 7.6 wt. %, low cost and high abundance. However, the use of  $MgH_2$  as hydrogen storage material is precluded by its high thermodynamic stability and the poor rates of its hydrogen release/uptake reactions, especially at temperatures below 300 °C [2]. An alternative to change the reaction paths and the thermodynamic properties of  $MgH_2$  is its combination with other hydrides such as  $LiBH_4$ . The  $2LiBH_4+MgH_2$  stoichiometric mixture (Li-RHC: Lithium reactive hydride composite) reacts via the formation of reversible phases:  $2LiBH_4+MgH_2 \rightleftharpoons 2LiH+MgB_2+4H_2$ . Li-RHC has larger theoretical gravimetric capacity of 11.45 wt. %  $H_2$ . However, due to kinetic constrains, the hydrogenation-dehydrogenation processes are sluggish and take place at relatively high temperature [3]. The kinetic properties of  $MgH_2$  and Li-RHC can be improved by the addition of nanostructured additives. In this work, nanosized additives added to  $MgH_2$  and Li-RHC are characterized via transmission electron microscopy (TEM). The aim is to understand the role of the additives on sorption kinetics of the investigated hydride systems. Additives such as Ti and FeTi improve noticeably the reactivity of  $MgH_2$ . This effect is mainly attributed to the nanosized nature of the intermetallic FeTi (Fig. 1A) and Ti (Fig. 1D), with  $Pm3m$  and  $Im3m$  space groups (s.g.) respectively. Moreover, in comparison with Ti, the intermetallic FeTi achieves a better dispersion, smaller nanoparticle sizes and largely homogenous distribution throughout the  $MgH_2$  matrix (Fig. 1B, 1C, 1E and 1F), which might be ascribed to a synergetic effect of Fe and Ti. In the case of the Li-RHC, fluorine additives such as  $NbF_5$  and  $TiF_4$  react with the hydrides mixture to form *in-situ* nanometric boride compounds ( $NbB_2$  and  $TiB_2$ ) with hexagonal structure (s.g.=  $P6/mmm$ ), as displayed in Fig. 2A and 2D. Size, distribution and composition of these boride species in the Li-RHC are responsible for enhanced hydrogen absorption-desorption rates (kinetic behavior). The Li-RHC+ $NbF_5$  system exhibits better kinetic behavior than the Li-RHC+ $TiF_4$  system. Fig. 2B, 2C, 2E and 2F show dark field (DF) images and particle size distribution of the boride species. As seen the  $NbB_2$  particles presents smaller average size and range of sizes than  $TiB_2$ . Additionally, the distribution of nanosized particles of  $NbB_2$  throughout the Li-RHC matrix is more homogenous than for  $TiB_2$ . Hence, the enhanced kinetic behavior of the Li-RHC+ $NbF_5$  accounts for the smaller size and efficient distribution of the  $NbB_2$  nanoparticles. In summary, the information gained by TEM was helpful to have a deeper insight into effects of the additives on the investigated hydride systems and to optimize solid state hydrogen storage system for practical applications.

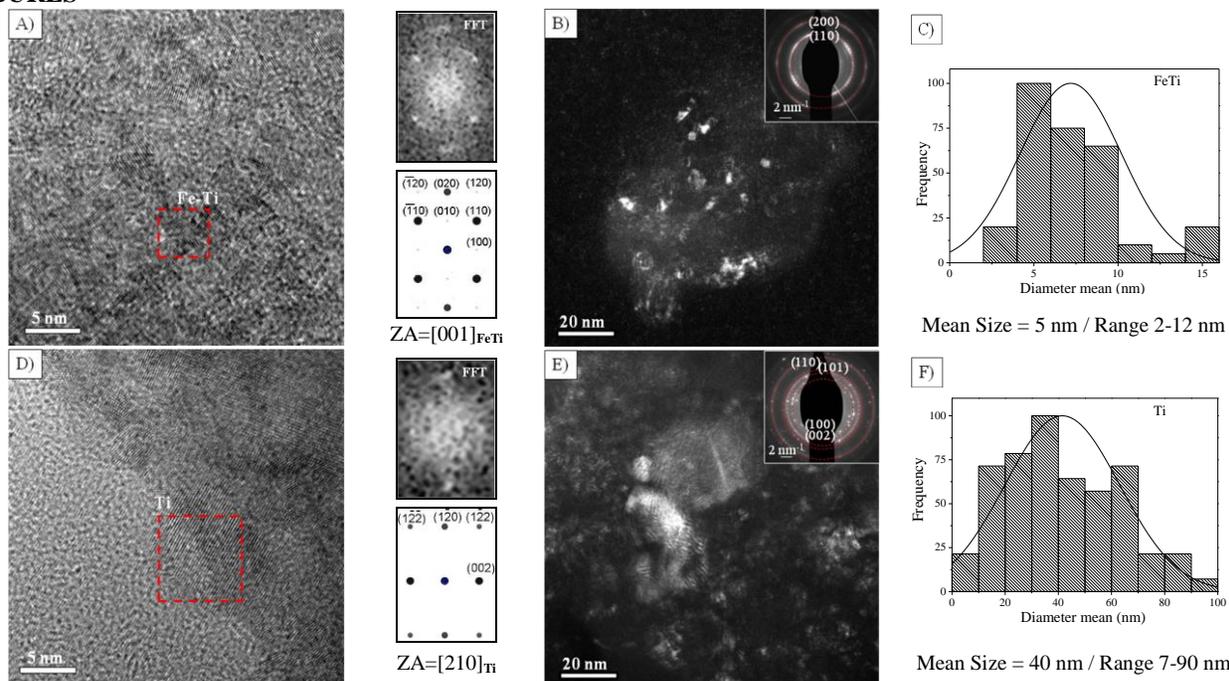
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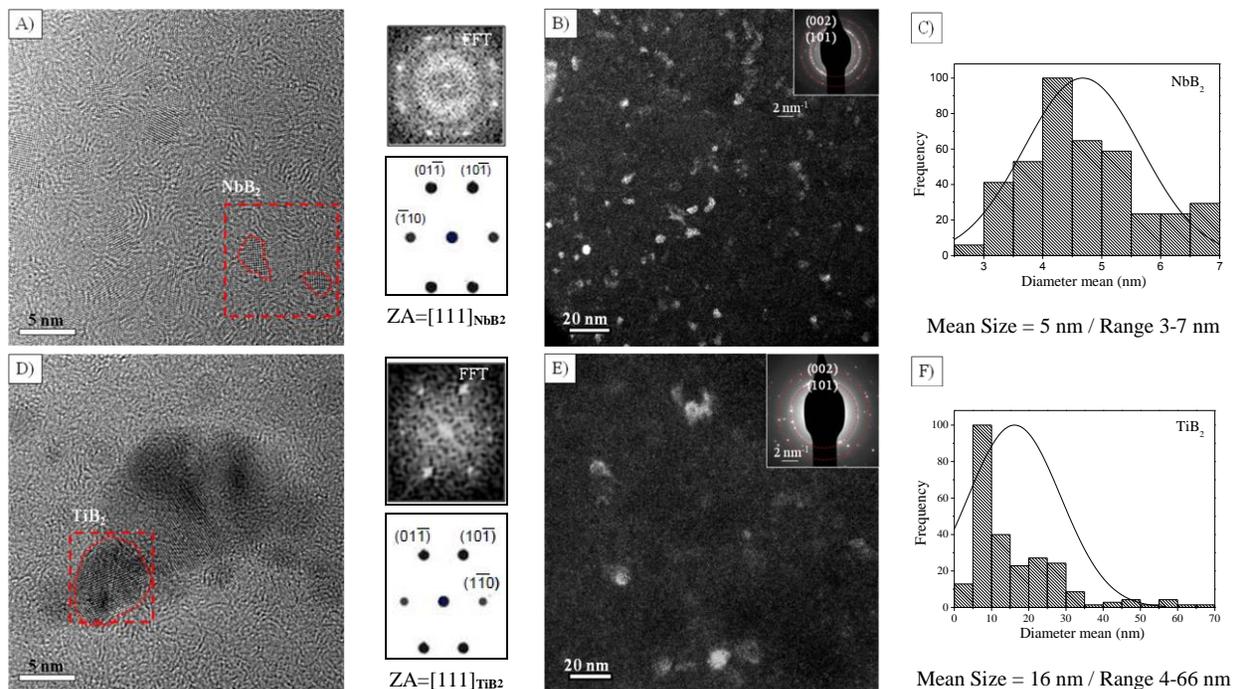
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**FIGURES**



**Figure 1:** A and D present High Resolution (HRTEM) images from FeTi and Ti particles, respectively. This was verified by comparing their Fast Fourier Transform (FFT) with diffraction patterns (DP) simulated by JEMS software. B and E show DF images obtained from those electrons that diffract generating the circled rings in the DP (upper-right inset). C and F condense the mean size and size distribution data obtained by measuring the particles highlighted in B and E.



**Figure 2:** A, D: HRTEM images on NbB<sub>2</sub> and TiB<sub>2</sub> particles, respectively. Structure and Zone Axis orientation was obtained from comparison between FFT and simulated DPs. B, E: DF obtained by selecting the rings shown in upper-right inset. C, F: mean size and size distribution of particles.