

Experiment title:	Powder diffraction line broadening study of Laves phases (Zr_xTi_{1-x})(Mn,Ni,Cr) ₂ after hydrogen absorption-desorption cycling. Implications on the cycle life of hydrogen storage tanks for fuel cell supply.	Experiment number: 01-01-603
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Numerous intermetallic compounds are known for their exceptional ability to react with hydrogen to form metal hydrides with high reversibility and high hydrogen storage density. Among them, LaNi₅ and substitutional derivatives have been studied especially for their possible use as electrode materials in nickel-metal hydride (Ni-MH) batteries. Zirconium or titanium Laves phases (AB₂, A = Zr, Ti and B = Mn, Ni, V) with C14 (hexagonal MgZn₂ type, $P6_3/mmc$) or C15 (cubic MgCu₂ type, $Fd\cdot3m$) structure possess even larger hydrogen storage capacity exceeding 1 hydrogen per metal atom. While their application as low density and safe materials for hydrogen gas storage has been investigated and is commercially attracting [1], their use as electrode material is hindered by difficult activation and high corrosion in the electrolytic medium [2].

Besides sensitivity to impurities, kinetics and heat transfer problems, one of the major drawbacks of metal hydrides is their degradation as a function of prolonged hydrogen absorption and desorption cycling [3]. For LaNi₅ derived compounds, hydrogen insertion leads to the creation of defects (mainly dislocations) originating from the large volume expansion accompanying the formation of the hydride compound. Dislocation accumulation leads to deterioration of the crystallinity and decrease of the storage capacity.

Dislocation structure has been previously characterized by the study of powder diffraction line broadening in previous SNBL experiment [4]. The aim of the present work was to perform the same type of work on AB₂ compounds.

Four samples were synthesized with suitable compositions for hydrogen storage and

crystallizing in the two forms of the Laves phases: C15 ($\text{ZrMn}_{0.71}\text{Ni}_{1.21}\text{V}_{0.22}$ (#1) and $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{Mn}_{0.71}\text{Ni}_{1.21}\text{V}_{0.22}$ (#2)) and C14 ($\text{Zr}_{0.8}\text{Ti}_{0.2}\text{MnNi}_{0.8}\text{V}_{0.2}$ (#1) and $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{Mn}_{0.9}\text{Ni}_{0.8}\text{V}_{0.3}$ (#2)). They were characterized by the synchrotron powder diffraction before and after 15 hydrogenation cycles.

Contrary to what occurs in LaNi_5 derived compounds, the broadening is found to be essentially isotropic. In a first approach, it can be analyzed by Williamson-Hall plots of the line widths obtained after Rietveld refinement of the diffraction patterns.

All samples show an increase of the line broadening induced by the hydrogenation (Fig.1). Preliminary analysis indicate that the line broadening in the cubic C15 compounds is much lower than in the hexagonal C14 compounds which contains important microstrains (#1 and #2) or a smaller mean apparent size of the particles (#1). If we compare the two C14 samples, the decrease of the particle size induced by hydrogenation is reduced with the increase of V quantity on the B site.

The non-cycled C15 compound #1 shows a larger slope than the three others non-cycled compounds (C15 #2, C14 #1 et C14 #2), which is probably related with the existence of a pronounced inhomogeneity of the metallic phase. This makes difficult to evaluate the effect of Ti substitution on the A site of C15 compounds after absorption-desorption cycling. In order to check the absence of anisotropic broadening and with the aim of modelling the observed line width, further individual peak profile fitting is in progress.

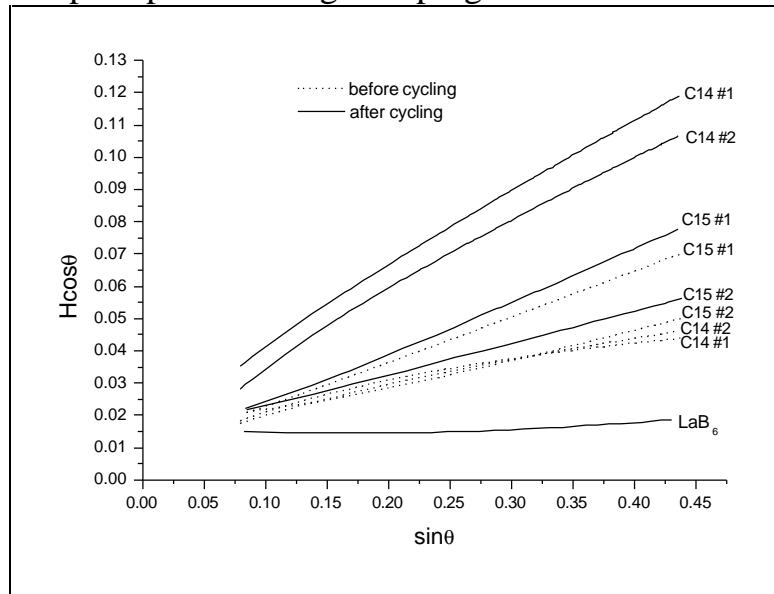


Fig. 1: Williamson-Hall plot of the diffraction line broadening in the different AB_2 -type compounds. H is a diffraction line full width at half of maximum in deg 2θ .

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2. Cuevas, F., J.-M. Joubert, M. Latroche, and A. Percheron-Guégan, *Applied Physics A* **72** (2001) 225-238.
3. Joubert, J.-M., M. Latroche, R. Cerny, A. Percheron-Guégan, and K. Yvon, *Journal of Alloys and Compounds*, **330-332** (2002) 208-214.
4. Cerny, R., J.-M. Joubert, M. Latroche, A. Percheron-Guégan, and K. Yvon, *Journal of Applied Crystallography*, **33** (2000) 997-1005.