

## Supplementary Information

### How 10 at% Al addition in the Ti-V-Zr-Nb high entropy alloy changes the hydrogen sorption properties?

Jorge Montero<sup>1\*</sup>, Gustav Ek<sup>2</sup>, Laetitia Laversenne<sup>3</sup>, Vivian Nassif<sup>3</sup>, Martin Sahlberg<sup>2</sup>, Claudia Zlotea<sup>1\*</sup>

<sup>1</sup>*Univ Paris Est Créteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France*

<sup>2</sup>*Department of Chemistry - Ångström Laboratory, Uppsala University, Box 523, SE-75120 Uppsala, Sweden*

<sup>3</sup>*University Grenoble Alpes, CNRS, Institut Néel, 38000 Grenoble, France*

\* Corresponding authors: [claudia.zlotea@icmpe.cnrs.fr](mailto:claudia.zlotea@icmpe.cnrs.fr) and [ing.monteroj@gmail.com](mailto:ing.monteroj@gmail.com)

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Figure SI1. XRD pattern comparison between the quaternary  $\text{Ti}_{0.325}\text{V}_{0.275}\text{Zr}_{0.125}\text{Nb}_{0.275}$  (top) and the quinary  $\text{Al}_{0.10}\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}$  (bottom) alloys as-cast by arc melting technique.

Figure SI2. Pressure composition isotherm of  $\text{Al}_{0.10}\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{H}_{1.6}$  measured at 100 °C. Sample activated at 340 °C under dynamic vacuum for 2 hours.

Figure SI3. *In-situ* neutron diffraction of  $\text{Ti}_{0.325}\text{V}_{0.275}\text{Zr}_{0.125}\text{Nb}_{0.275}\text{D}_{1.8}$  under a heating ramp of 1 °C/min while under dynamic vacuum, along with the corresponding desorption profile on the right.

Figure SI4. Reversible hydrogen absorption capacity at 25 °C of  $\text{Ti}_{0.325}\text{V}_{0.275}\text{Zr}_{0.125}\text{Nb}_{0.275}$  upon 20 cycles. The cycling evaluation consisted in measuring the hydrogen capacity at room temperature followed by complete hydrogen desorption. The latter step was done by heating at 400 °C while evacuating under secondary vacuum ( $10^{-5}$  mbar) for 10 hours.

Figure SI5. Chemical mapping (SEM-EDX) of the hydride  $\text{Al}_{0.10}\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{H}_{1.5}$  after 20 hydrogen absorption/desorption cycles. Similar Al-Zr-rich and Al-Zr-poor regions can be observed as the initial alloy.

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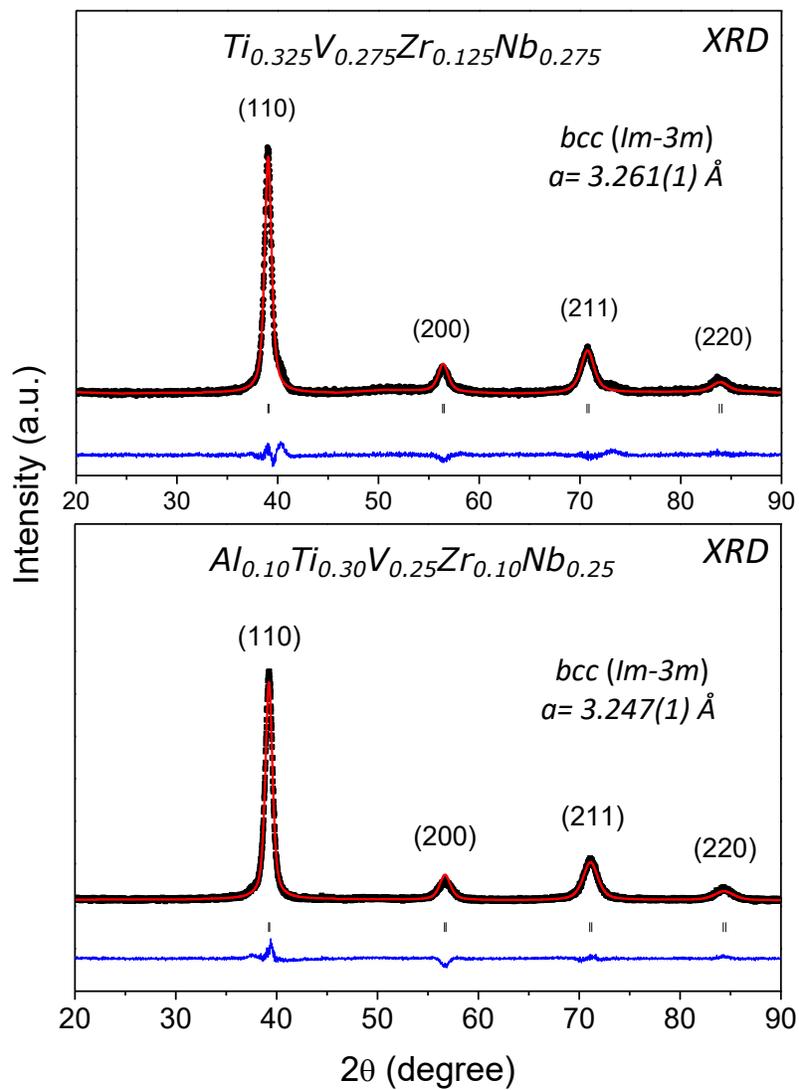


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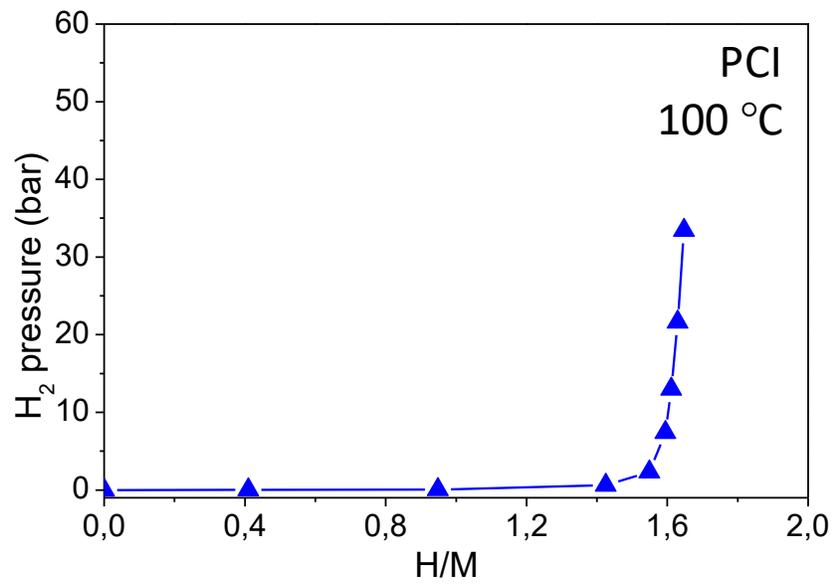


Figure S13. *In-situ* neutron diffraction of  $\text{Ti}_{0.325}\text{V}_{0.275}\text{Zr}_{0.125}\text{Nb}_{0.275}\text{D}_{1.8}$  under a heating ramp of  $1\text{ }^\circ\text{C}/\text{min}$  while under dynamic vacuum, along with the corresponding desorption profile on the right.

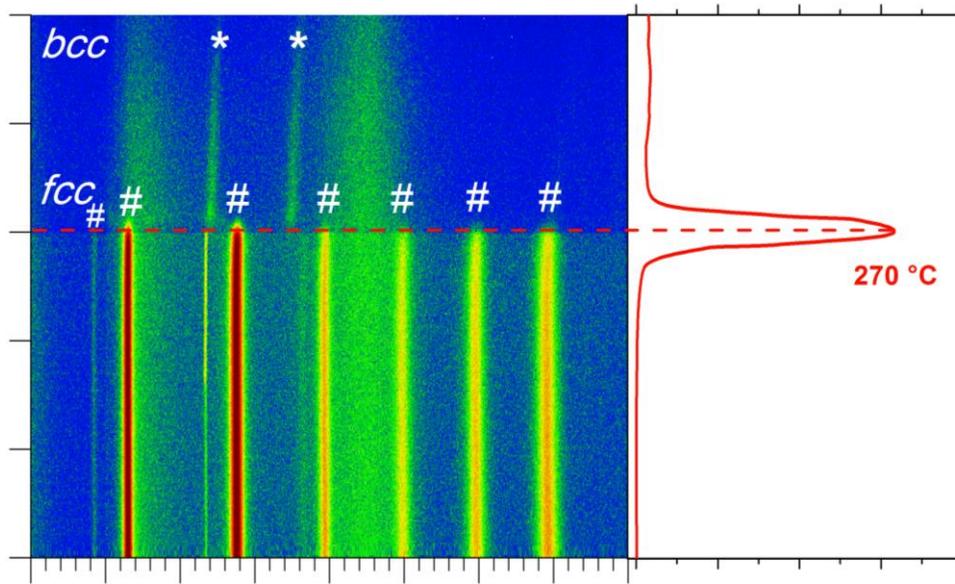


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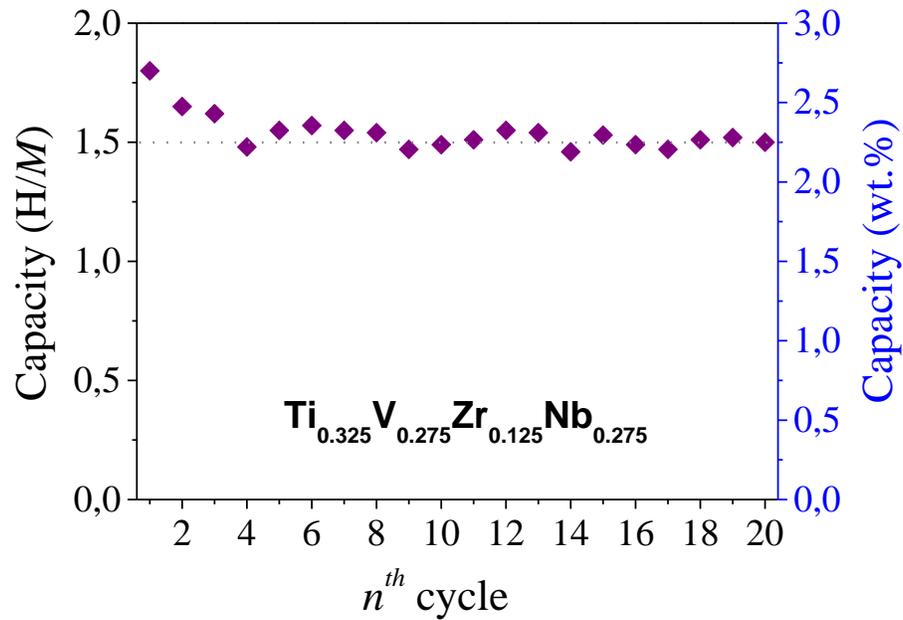


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