Experimental report

24/01/2024

Proposal: 5-25-284 **Council:** 10/2022

Title: In situ hydrogen desorption study from high entropy hydrides: effect of addition of non-absorbing elements (Al, Cr, Mo) in the TiVNb alloy

Research area: Materials

This proposal is a new proposal

Main proposer: **Claudia ZLOTEA**

Experimental team: Nayely PINEDA ROMERO
Claudia ZLOTEA
Faye GREAVES

Local contacts: Vivian NASSIF

Samples: (TiVNb)90Al5Cr5
(TiVNb)90Al5Mo5
(TiVNb)80Al10Cr10
(TiVNb)80Al10Mo10
(TiVNb)80Al5Cr15
(TiVNb)80(Cr20-xFex) x=2, 5, and 7
TiZrNbHf)80(V20-xTax) x=0, 5, 10, 15, and 20

Instrument	Requested days	Allocated days	From	To
D1B	4	4	06/04/2023	10/04/2023

Abstract:

High entropy alloys are a new class of materials with exciting hydrogen storage properties. We propose here to study the phase transition during hydrogen thermal desorption from the (TiVNb)100-x(A)x alloys where A = Al, Cr and Mo. The hydride phases with A = Cr and Mo adopt fcc lattice whereas, the hydrides containing Al have mainly a bct structure. It is not clear, yet which parameters influence the formation of one or the other lattices: chemical composition, steric effects, lattice strain or preferential occupation of hydrogen in specific interstitials etc. Thus, neutron diffraction studies are essential to elucidate the phase transformation leading to the formation of either fcc or bct dihydride phases as function of A element (Al, Cr and Mo) and to localize the deuterium atoms in the interstitial sites. These results will help understanding the effect of A element addition and will guide further research on high entropy alloys for hydrogen storage.

Report experiment no 5-25-284

In situ hydrogen desorption study from high entropy dihydrides: effect of addition of non-absorbing elements (Al, Cr, Mo) in the TiVNb alloy

We have initially proposed to perform in situ neutron diffraction on seven samples in the $(TiVNb)_{100-x}A_x$ high entropy alloys (*A* = Al, Cr and/or Mo; x = 0, 5 and 10) foreseen for solid-state hydrogen storage:

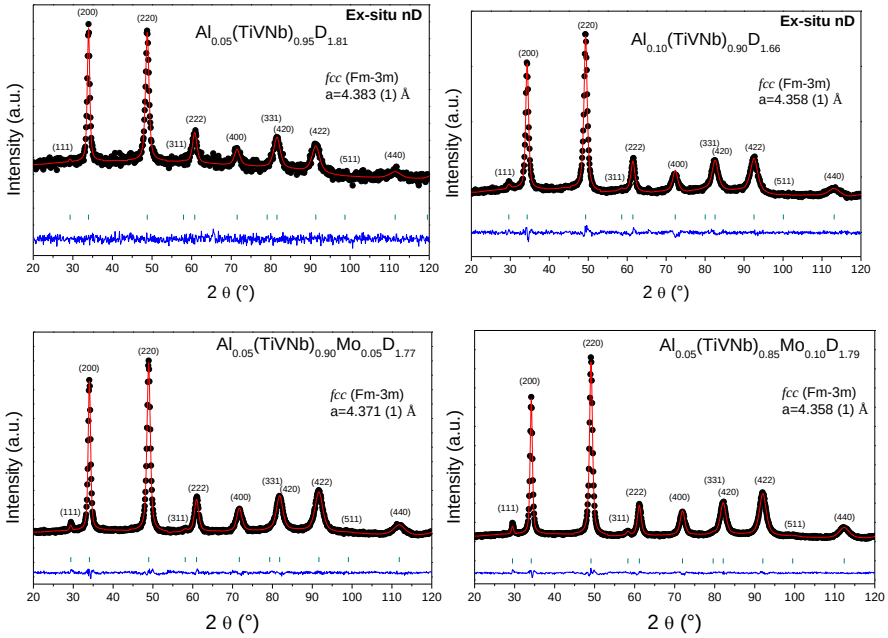
(i) to elucidate the phase transformation leading to the formation of either fcc or bct dihydride phases as function of additional elements (Al, Cr and Mo),

(ii) to localize the deuterium atoms inside the available interstitial sites and

(iii) to clarify the correlation between the preferential deuterium occupancy of the interstitial sites and the formation of a bct dihydride in case of Al containing HEAs.

The evaluation committee suggested us to focus on fewer samples. Thus, during the experiment we thoroughly investigated by in situ and ex situ neutron diffraction 5 samples in this series: $(TiVNb)_{95}Al_5$, $(TiVNb)_{90}Al_{10}$, $(TiVNb)_{90}Al_5Cr_5$, $(TiVNb)_{90}Al_5Mo_5$ and $(TiVNb)_{85}Al_5Mo_{10}$.

1) Ex situ neutron diffraction patterns have been acquired at room temperature on fully deuterated samples (figure 1). These experiments are necessary to localize the deuterium into the interstitial sites of the final dihydride. Rietveld refinements have been used for structural analysis.



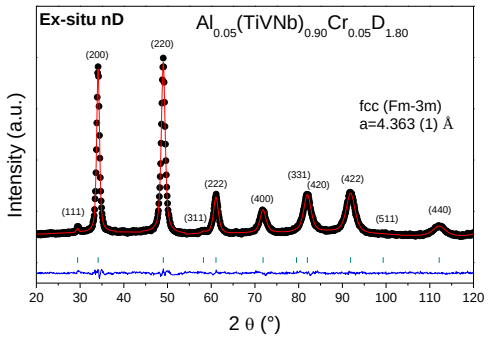
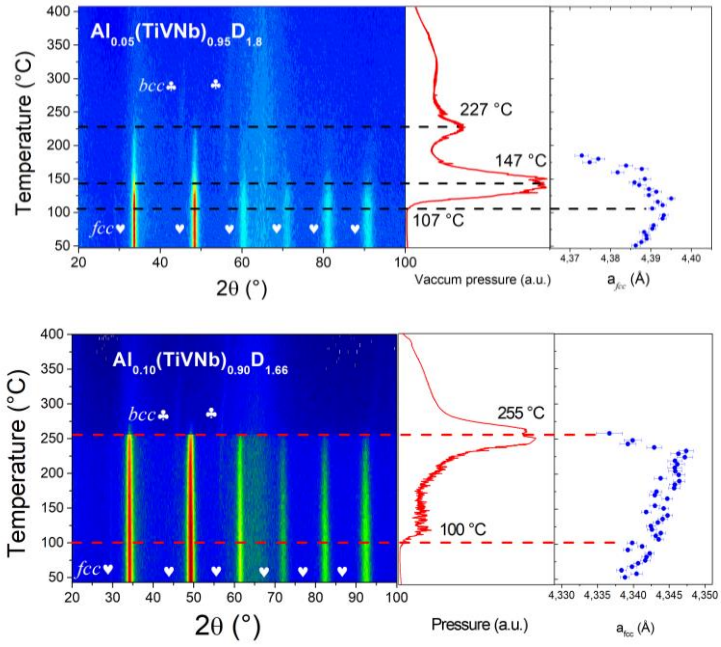
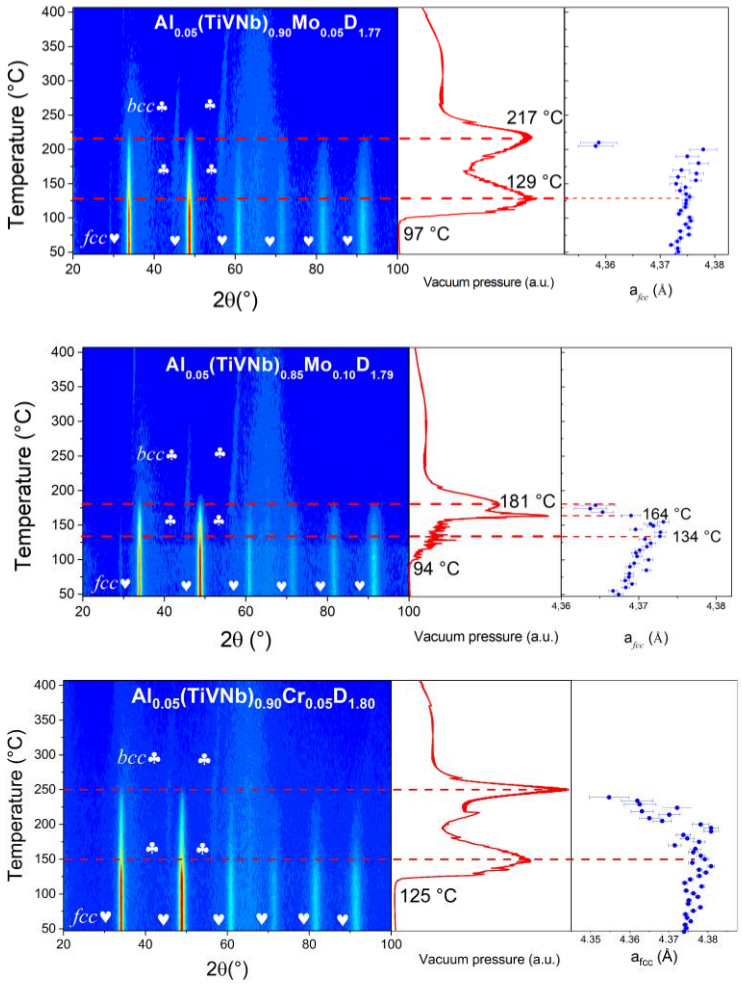


Figure 1. Ex situ neutron diffraction patterns and related Rietveld refinements.

Finaly, Rietveld refinements have proven that all deuterated samples adopt a fcc (Fm-3m) lattice with deuterium atoms located into the tetrahedral interstitial sites.

2) In situ neutron diffraction have been acquired starting from fully deuterated samples during constant heating with 1°C/min temperature rate under dynamic vacuum. The evolution of the pressure of evolved gas was continuously recorded by a vacuum gauge during the desorption experiments. Due to the modest resolution of in situ patterns, structural analysis was performed by using Le bail fitting to determine the lattice parameter evolution with temperature (Figure 2).





All deuterated samples desorb deuterium upon heating following several steps, as illustrated in the desorption profile diagrams. Obviously, the presence of additional elements drastically influences the temperature of desorption: the addition of Mo shifts the desorption profile to lower temperature.

The lattice parameters initially undergo a thermal expansion followed by shrinking due to desorption. A phase transition occurs in all sample to a bcc phase those diffraction peaks are hardly visible due to the negligeable coherent scattering length of the metallic network (1-3 fm) as compared to the respective deuteride (14-15 fm).

One publication was accepted in 2023: “Large Destabilization of (TiVNb)-Based Hydrides via (Al, Mo) Addition: Insights from Experiments and Data-Driven Models” *CS Appl. Energy Mater*. 2023, 6, 24, 12560–12572, 10.1021/acsaem.3c02696

One other publication is in preparation for a submission in February 2024.