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FunHy Newsletter

Who and where?

Magnus Moe Nygård, Gustav Ek, Dennis Karlsson, Martin Sahlberg, Magnus H. Sørby and Bjørn C. Hauback has recently published the article *Hydrogen storage in high-entropy alloys with varying degree of local lattice strain* in International Journal of Hydrogen Energy (DOI: <https://doi.org/10.1016/j.ijhydene.2019.03.223>).

Why?

The article is based on a recent observation where TiVZrNbHf, a body-centered cubic (bcc, $Im\bar{3}m$) high-entropy alloy (HEA), was able to absorb hydrogen so that the hydrogen-to-metal ratio reaches $[H]/[M] = 2.5$ [1]. In this process, the structure changes to a *pseudo* face-centered cubic ($Fm\bar{3}m$) structure with a slight body-centered tetragonal (bct, $I4/mmm$) distortion. Such a high hydrogen-to-metal ratio has never before been observed in metal hydrides that are formed exclusively from transition metals. The result suggests that all the tetrahedral- and about half of the octahedral interstices are occupied by hydrogen. This is rarely observed in binary metal hydrides such as TiH₂, ZrH₂ or PdH where H occupies either the tetrahedral or octahedral interstices. This could mean that the so-called *Switendick criterion*, which states that the hydrogen atoms should be at least 2 Å apart, is violated. It was suggested that the “[...] the built in strain in an HEA could be the driving force to open up new interstitial sites for hydrogen” [1]. If a similar effect could be observed in other HEAs, it could be possible to determine a critical value for the local lattice strain δr that is necessary to enable H to occupy the octahedral and tetrahedral sites simultaneously. Thus, the hydrogen storage capacity of the materials could be enhanced.

How?

To investigate the hypothesis outlined above, the authors have synthesized a series of high-entropy alloys with stoichiometric compositions TiVZr_zNbTa_{1-z}, $z = 0, 0.15, 0.50, 0.74, 1.0$ and TiVZr_{1+z}Nb, $z = 0.20, 0.50, 0.75, 1.0$. All of these alloys assume bcc structures and form fcc metal hydrides through a gas-solid reaction. As Zr is significantly larger than the other atoms, the local lattice strain can be tuned by altering the Zr-content in the alloy. The most Zr-rich

systems have local lattice strain larger than TiVZrNbHf, while the local lattice strain in the Zr-free TiVNbTa is much less. Nevertheless, the hydrogen-to-metal ratios are close to, but never larger than 2. No correlation between δr and the $[H]/[M]$ can therefore be obtained. The hydrides are stabilized when the Zr-content increases. Furthermore, the most Zr-rich systems phase separate when they are heated. The result is then a combination of two bcc phases, one with a larger and one with a smaller unit cell than that of the

original. There are indications that the largest is Zr-rich, while the smallest is Zr-poor. The phase separation has been traced with *in situ* synchrotron radiation powder X-ray diffraction. This has revealed that the largest bcc phase forms from an intermediate C15 Laves phase ($Fd-3m$) that forms after the phase separation has occurred.

[1] Sahlberg, Martin, et al. "Superior hydrogen storage in high entropy alloys." *Scientific reports* 6 (2016): 36770.

FunHy webpage: <http://inano.au.dk/about/research-groups/nano-energy-materials/projects/neutrons-for-multi-functional-hydrides-funhy/>

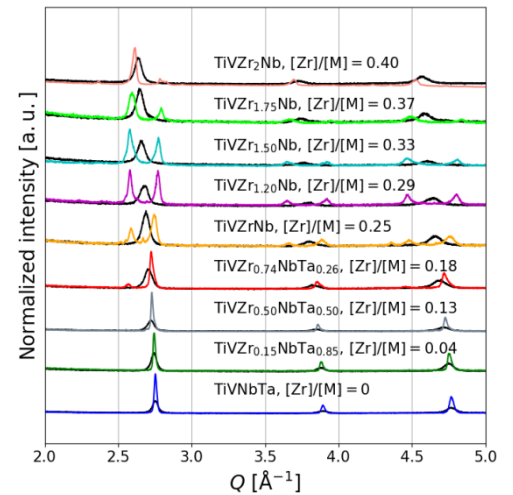


Figure 1: Cu-K α PXD patterns of the as cast alloys TiVZr $_z$ NbTa $_{1-z}$ and TiVZr $_1$ p $_z$ Nb (black) and the alloys obtained after desorbing the hydrides at 1000 °C in the TG/DSC (coloured).