Supplementary Information

TiVNb-based high entropy alloys as catalysts for enhanced hydrogen storage in nanostructured MgH_2

Jingxi Zhang[a,b], Huang Liu[b,c], Chengshang Zhou[*,b,c], Pei Sun[*,b], Xueyi Guo[*,a], Zhigang Zak Fang[b]

a School of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, P.R. China

b Department of Materials Science and Engineering, The University of Utah, Salt Lake City, Utah 84112-0114, United States

c State Key Laboratory for Powder Metallurgy, Central South University, Changsha, Hunan 410083, P.R. China

[*]Corresponding author

E-mail addresses: chengshang.zhou@utah.edu; pei.sun@utah.edu; xyguo@csu.edu.cn

For the HEAs, the empirical parameters of average atomic size mismatch (δ), valance electron concentration (VEC) and electronegativity differences ($^{\Delta\chi_{Allen}}$) are usually used to determine the phase structure formation and the stability[1-3]. These parameters can be determined using the following equations:

$$\delta = \sqrt{\sum c_i\left(1 - \frac{r_i}{\bar{r}}\right)^2} \times 100 \quad (1)$$

$$VEC = \sum c_i VEC_i \quad (2)$$

$$\Delta\chi_{Allen} = \sqrt{\sum_{i=1}^{n} c_i(\chi_i - \bar{\chi})^2}\bar{\chi} \quad (3)$$

where c_i, r_i, VEC_i and χ_i stood for the atom fractions, the atomic radius, valence electron concentration and electronegativity of element i. $\bar{r}$ and $\bar{\chi}$ represented the average atomic radius and the average electronegativity of HEA. The physicochemical parameters essential for the estimation of the above parameters were obtained from the literature [4] [5] and provided in Table S1.

Table S1 Atomic radius, electronegativities and VEC for selected of elements.

Element	Atomic radius (Å)	Electronegativity	VEC
Ti	1.46	1.54	4
V	1.32	1.63	5
Nb	1.43	1.6	5
Zr	1.6	1.33	4
Fe	1.24	1.83	8
Cr	1.25	1.66	6
Ni	1.25	1.91	10

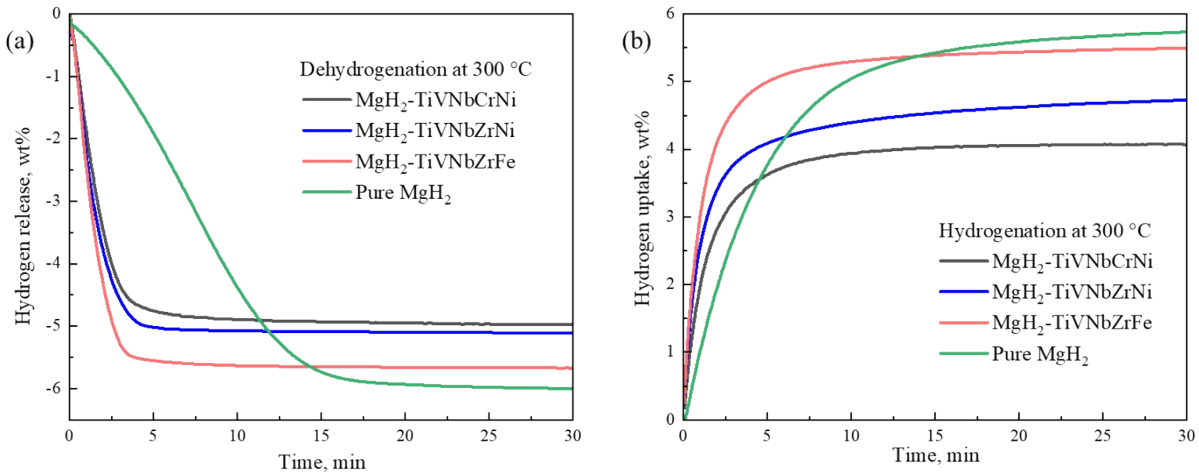

Figure S1 The isothermal dehydrogenation (a) and hydrogenation (b) curves of MgH_2-HEAs and pure MgH_2 at 300℃.

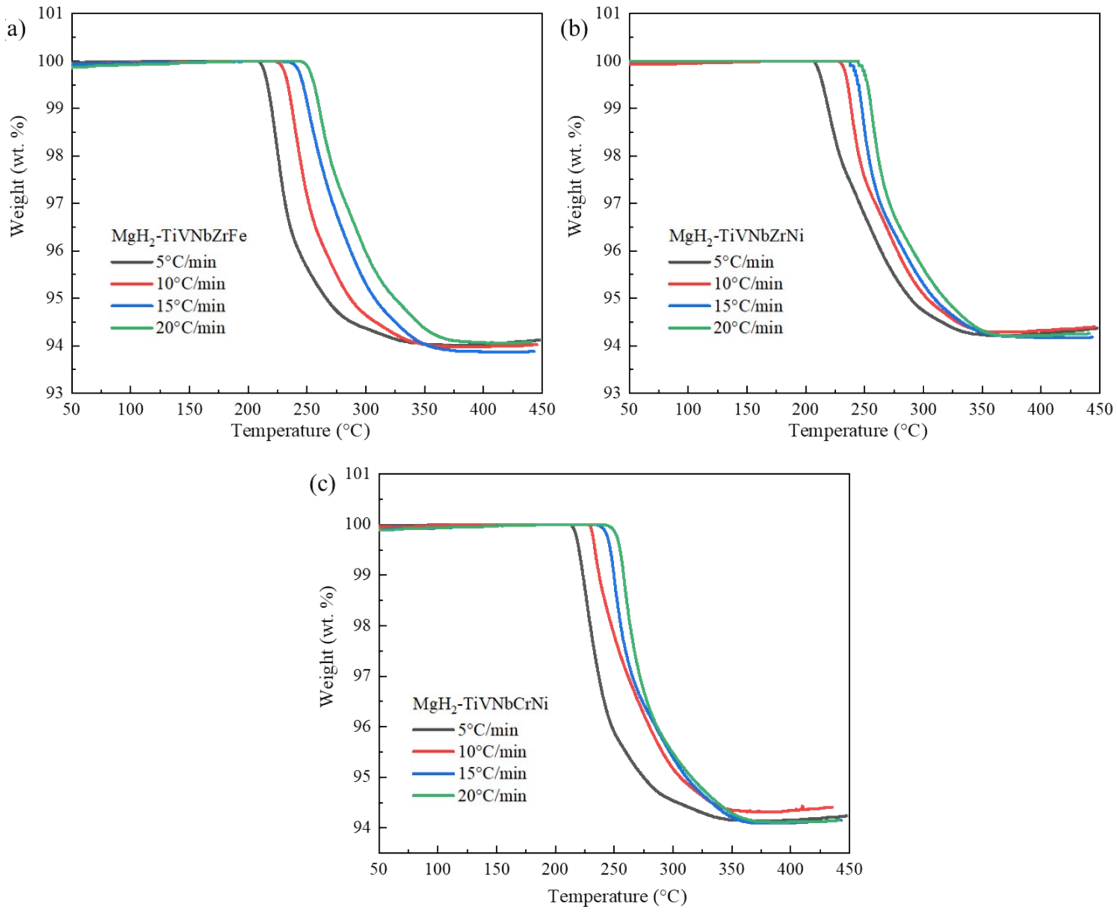

Figure S2 The TGA results for the (a) MgH_2-TiVNbZrFe, (b) MgH_2-TiVNbZrNi and (c) MgH_2-TiVNbCrNi under various heating rates.

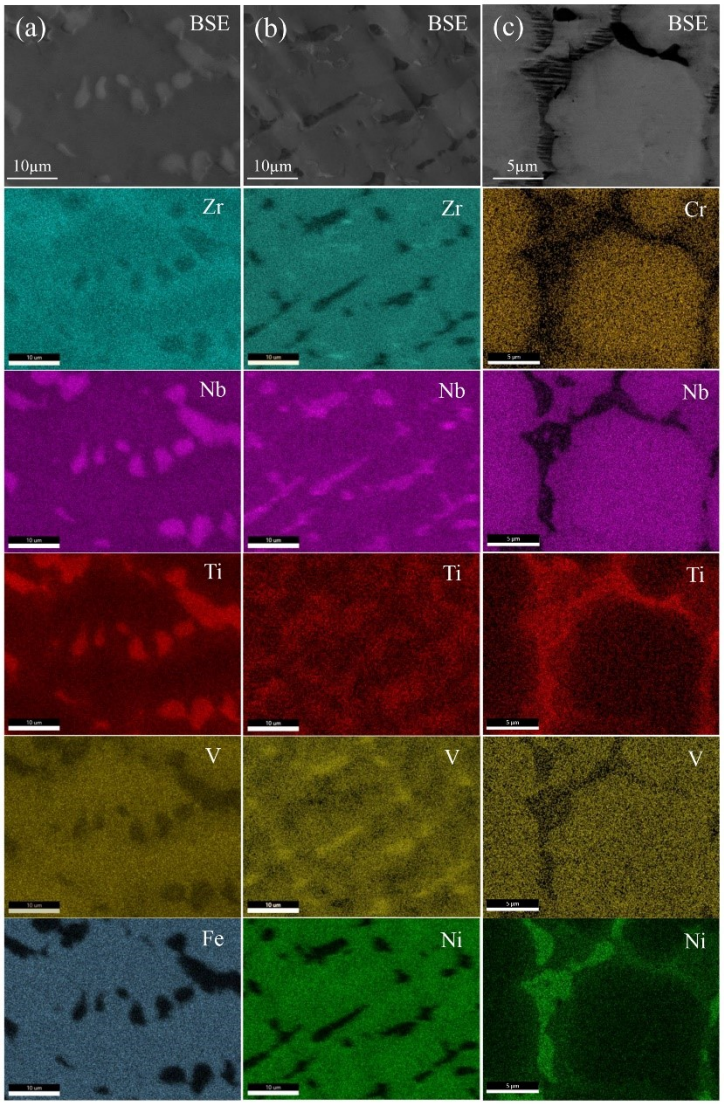

Figure S3 The BSE and corresponding EDS elemental mappings for the (a) TiVNbZrFe, (b) TiVNbZrNi and (c) TiVNbCrNi

Reference

1 Zhang Y., Zhou Y. J., Lin J. P., Chen G. L. and Liaw P. K., *ADVANCED ENGINEERING MATERIALS*, 2008, **10**, 534-538.
2 Miracle D. B. and Senkov O. N., *Acta Materialia*, 2017, **122**, 448-511.
3 Guo S., Ng C., Lu J. and Liu C. T., *JOURNAL OF APPLIED PHYSICS*, 2011, **109**, 103505.
4 Mizutani U., Sato H., Inukai M., Nishino Y. and Zijlstra E. S., *Inorg Chem*, 2015, **54**, 930-46.
5 Mishra S. S., Yadav T. P., Srivastava O. N., Mukhopadhyay N. K. and Biswas K., *Journal of Alloys and Compounds*, 2020, **832**, 153764.