

Supplementary information

Compositional effects on the hydrogen storage properties in a series of refractory high entropy alloys

Claudia Zlotea^{1}, Anis Bouzidi¹, Jorge Montero¹, Gustav Ek² and Martin Sahlberg²*

*¹University Paris Est Créteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais,
France*

²Department of Chemistry – Ångström laboratory, Uppsala University, Uppsala, Sweden

**Corresponding author: claudia.zlotea@cnrs.fr*

Figure SI-1: XRD patterns ($\lambda = 1.5406 \text{ \AA}$) of the Ti-V-Zr-Nb-*M* alloys with *M* = Fe, Co, Ni and Cu prepared by arc melting.

Figure SI-2: XRD patterns recorded every 15 minutes during the BM process for the Ti-V-Zr-Nb-Fe alloy.

Figure SI-3: SEM chemical mapping and EDS results for $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{M}_{0.10}$ compositions with *M* = Mg, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Ta as well as the pristine quaternary alloy $\text{Ti}_{0.325}\text{V}_{0.275}\text{Zr}_{0.125}\text{Nb}_{0.275}$.

Figure SI-4: XRD patterns ($\lambda = 1.5406 \text{ \AA}$) of the Ti-V-Zr-Nb-*M* alloys with *M* = Fe, Co, Ni, Cu and Zn as well as the quaternary Ti-V-Zr-Nb composition prepared by RBM and desorbed following a pre-treatment under dynamic vacuum at 400 °C.

Figure SI-5: Kinetic curves recorded at 25 °C under 25-30 bar H₂ pressure for selected compositions.

Figure SI-6: Attempts to correlate the *bcc* lattice parameters to the VEC and the average atomic radius.

Figure SI-1: XRD patterns ($\lambda = 1.5406 \text{ \AA}$) of the Ti-V-Zr-Nb-*M* alloys with *M* = Fe, Co, Ni and Cu prepared by arc melting.

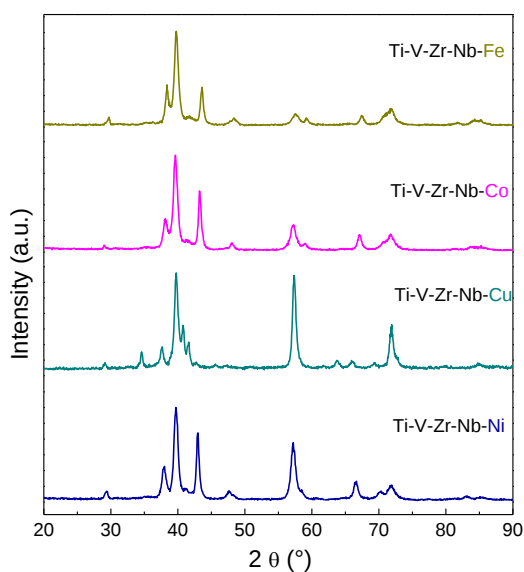


Figure SI-2: XRD patterns recorded every 15 minutes during the BM process for the Ti-V-Zr-Nb-Fe alloy.

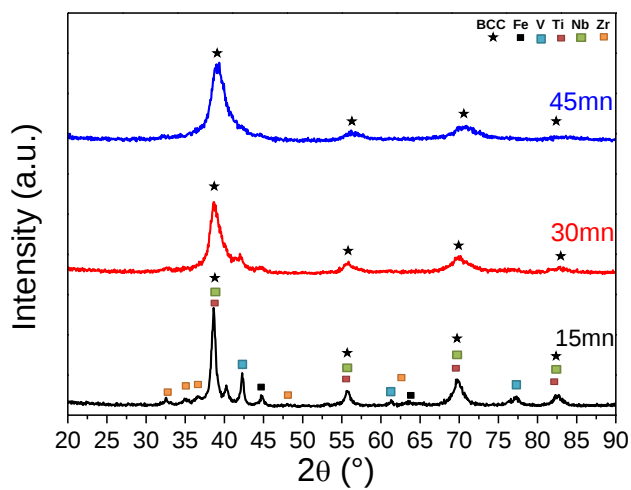
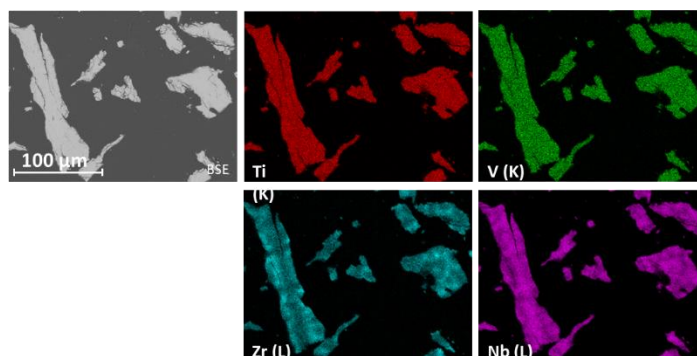


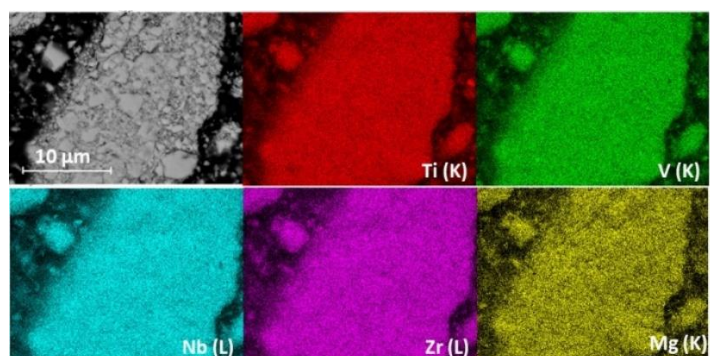
Figure SI-3: SEM chemical mapping and EDS results for $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{M}_{0.10}$ compositions with $M = \text{Mg, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Ta}$ as well as the pristine quaternary alloy $\text{Ti}_{0.325}\text{V}_{0.275}\text{Zr}_{0.125}\text{Nb}_{0.275}$.

1) $\text{Ti}_{0.325}\text{V}_{0.275}\text{Zr}_{0.125}\text{Nb}_{0.275}$ (AM)



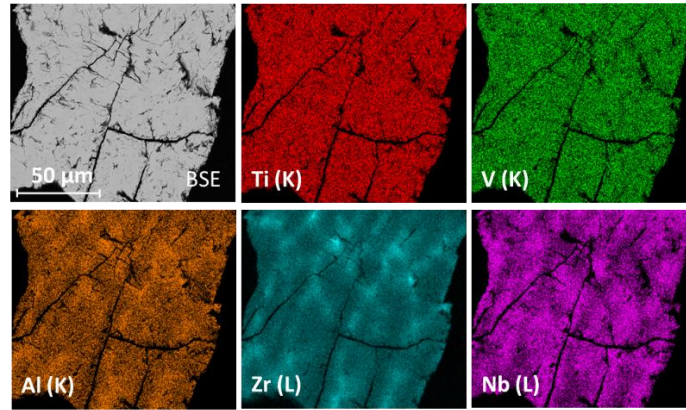
Region	Ti (at.%)	V (at.%)	Zr (at.%)	Nb (at.%)
Dendritic	32.1(0.3)	26.9(0.4)	10.8(0.8)	30.2(1.1)
Interdendritic	32.2(0.3)	25.5(0.4)	21.8(1.7)	20.5(1.4)
Overall	32.4(0.3)	27.1(0.4)	13.2(1.7)	27.3(1.4)
Nominal	32.5	27.5	12.5	27.5

2) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Mg}_{0.10}$ (RBM)



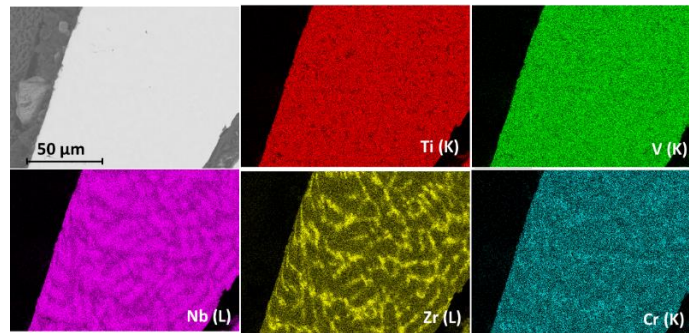
Region	Ti (at.%)	V (at.%)	Mg (at.%)	Zr (at.%)	Nb (at.%)
Overall	29.9(0.5)	24.3(0.8)	12.1(0.5)	9.8(0.4)	23.9(0.5)
Nominal	30	25	10	10	25

3) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Al}_{0.10}$ (AM)



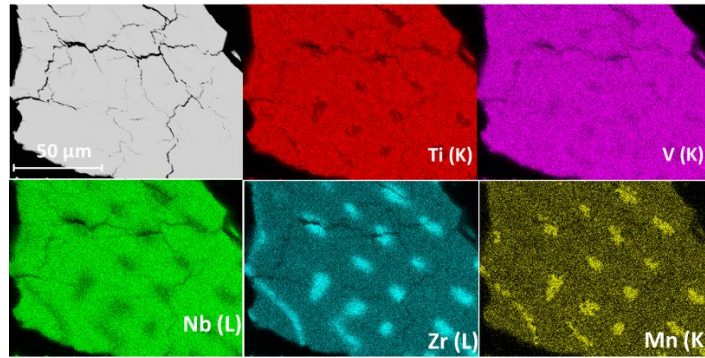
Region	Al (at.%)	Ti (at.%)	V (at.%)	Zr (at.%)	Nb (at.%)
Dendritic	9.2(0.4)	29.8(0.6)	24.7(0.7)	8.3(0.6)	28.0(0.5)
Interdendriti	12.1(0.6)	28.7(0.9)	22.6(1.2)	17.5(2.5)	19.1(1.6)
Overall	10.0(0.6)	29.5(0.9)	24.6(1.2)	10.8(2.5)	25.1(1.6)
Nominal	10	30	25	10	25

4) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Cr}_{0.10}$ (AM)



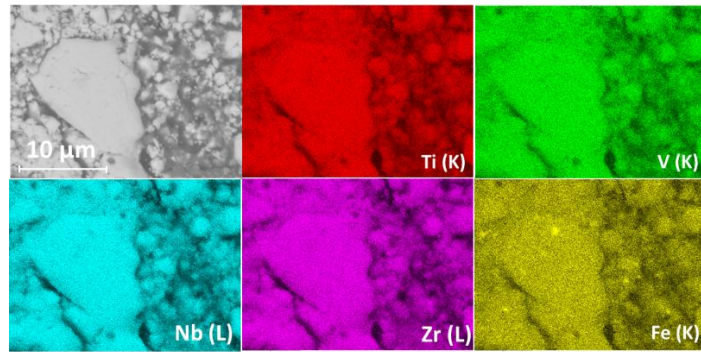
Region	Ti (at.%)	V (at.%)	Cr (at.%)	Zr (at.%)	Nb (at.%)
Dendritic	30.2(0.5)	25.1(0.4)	8.1(0.4)	5.8(0.5)	30.8(1.2)
Interdendritic	29.9(1.1)	23.4(0.7)	11.1(0.8)	18.5(1.5)	17.1(1.8)
Overall	30.5(1.1)	25.4(0.7)	9.5(0.8)	10.3(1.5)	24.3(1.8)
Nominal	30	25	10	25	10

5) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Mn}_{0.10}$ (AM)



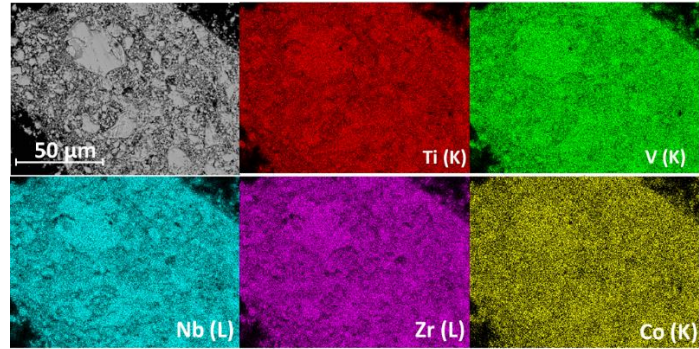
Region	Ti (at.%)	V (at.%)	Mn (at.%)	Zr (at.%)	Nb (at.%)
Dendritic	31.3(1.3)	26.3(0.5)	7.2(1.8)	8.3(0.8)	26.9(0.5)
Interdendritic	27.2(0.8)	24.3(0.7)	12.7(1.0)	15.9(1.5)	19.9(1.3)
Overall	30.6(1.3)	25.8(0.7)	9.1(1.8)	10.2(1.5)	24.4(1.3)
Nominal	30	25	10	10	25

6) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Fe}_{0.10}$ (RBM)



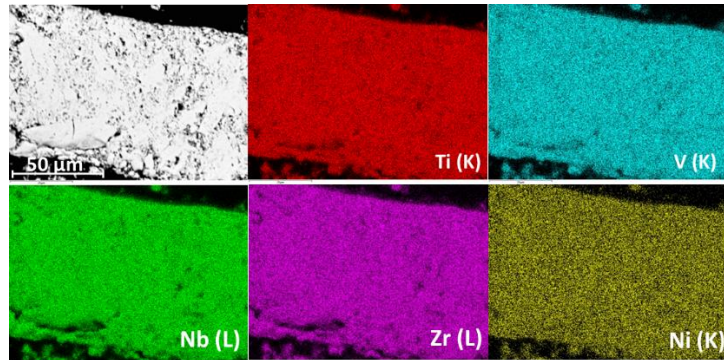
Region	Ti (at.%)	V (at.%)	Fe (at.%)	Zr (at.%)	Nb (at.%)
Overall	30.1(1.0)	24.2(1.3)	11.9(1.0)	9.4(0.4)	24.4(1.0)
Nominal	30	25	10	10	25

7) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Co}_{0.10}$ (RBM)



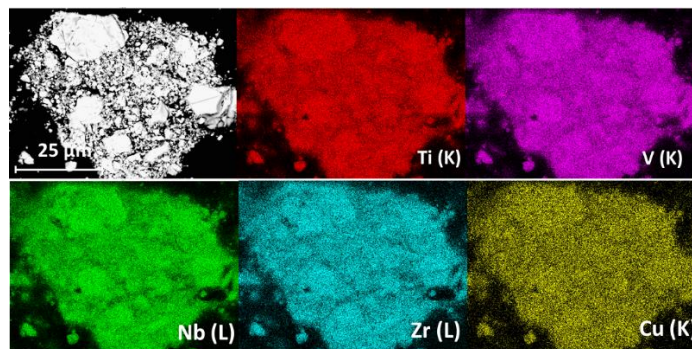
Region	Ti (at.%)	V (at.%)	Co (at.%)	Zr (at.%)	Nb (at.%)
Overall	29.9(0.7)	25.7(0.6)	9.6(0.4)	9.6(0.7)	25.2(0.7)
Nominal	30	25	10	10	25

8) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Ni}_{0.10}$ (RBM)



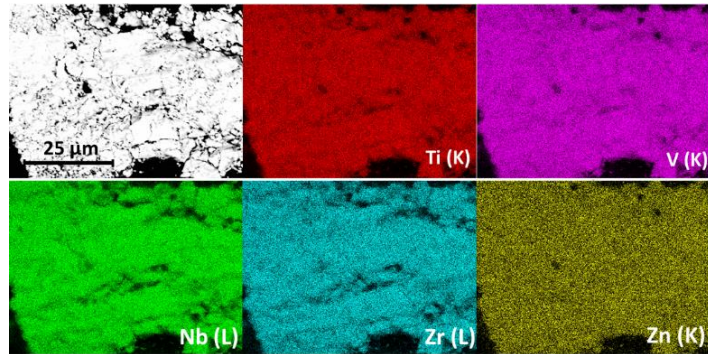
Region	Ti (at.%)	V (at.%)	Ni (at.%)	Zr (at.%)	Nb (at.%)
Overall	29.2(0.4)	24.1(0.7)	9.3(1.0)	10.6(0.4)	26.8(1.2)
Nominal	30	25	10	10	25

9) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Cu}_{0.10}$ (RBM)



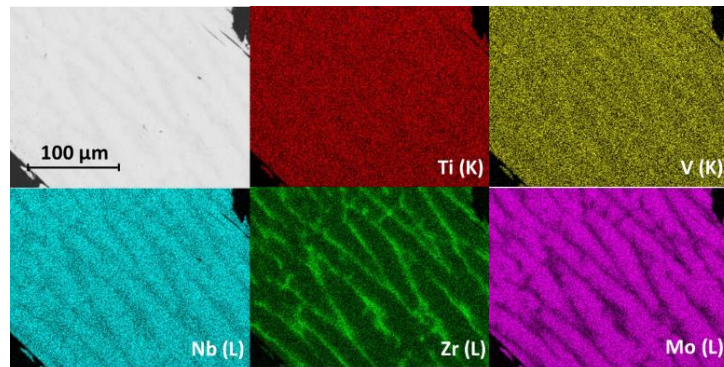
Region	Ti (at.%)	V (at.%)	Cu (at.%)	Zr (at.%)	Nb (at.%)
Overall	30.6(0.7)	25(0.6)	9.4(0.2)	9.7(0.4)	25.3(0.6)
Nominal	30	25	10	10	25

10) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Zn}_{0.10}$ (RBM)



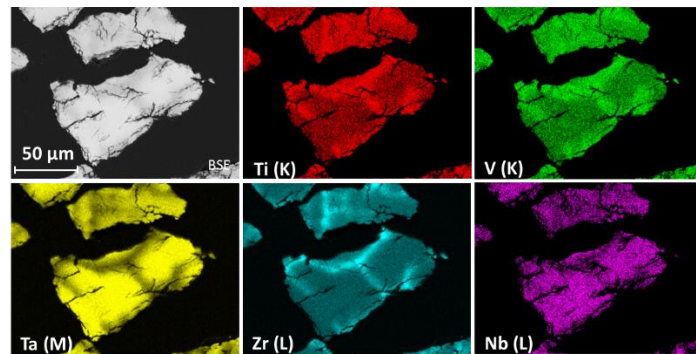
Region	Ti (at.%)	V (at.%)	Zn (at.%)	Zr (at.%)	Nb (at.%)
Overall	30.1(0.3)	24.7(0.6)	9.9(0.3)	9.8(0.3)	25.5(0.6)
Nominal	30	25	10	10	25

11) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Mo}_{0.10}$ (AM)



Region	Ti (at.%)	V (at.%)	Zr (at.%)	Nb (at.%)	Mo (at.%)
Dendritic	28.2(0.5)	22.9(0.2)	6.2(0.4)	29.8(0.7)	12.9(0.4)
Interdendritic	30.4(0.3)	25.5(0.4)	23.6(1.7)	15.9(2.4)	4.9(1.2)
Overall	30.1(0.5)	24.8(0.5)	10.3(1.7)	25.1(2.4)	9.7(1.2)
Nominal	30	25	10	25	10

12) $\text{Ti}_{0.30}\text{V}_{0.25}\text{Zr}_{0.10}\text{Nb}_{0.25}\text{Ta}_{0.10}$ (AM)



<i>Region</i>	<i>Ti (at.%)</i>	<i>V (at.%)</i>	<i>Zr (at.%)</i>	<i>Nb (at.%)</i>	<i>Ta (at.%)</i>
Dendritic	25.9(1.0)	20.3(0.7)	5.6(0.3)	32.2(0.7)	16(0.9)
Interdendritic	30.8(0.6)	25.6(1.1)	21.1(2.9)	17.9(1.3)	4.6(0.8)
Overall	28.5(1.0)	24.3(1.1)	9.7(2.9)	26.0(1.3)	11.5(0.9)
Nominal	30	25	10	25	10

Figure SI-4: XRD patterns ($\lambda = 1.5406 \text{ \AA}$) of the Ti-V-Zr-Nb-M alloys with $M = \text{Fe, Co, Ni, Cu}$ and Zn as well as the quaternary Ti-V-Zr-Nb composition prepared by reactive ball milling and desorbed following a pre-treatment under dynamic vacuum at 400 °C.

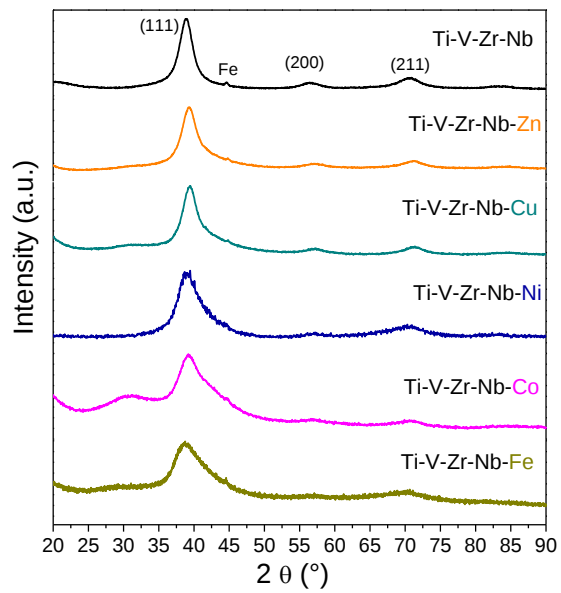


Figure SI-5: Kinetic curves recorded under 25-30 bar H_2 pressure at 25 °C for selected compositions: $Ti_{0.30}V_{0.25}Zr_{0.10}Nb_{0.25}M_{0.10}$ with $M = Mg, Al, Cr, Mo$ and Ta .

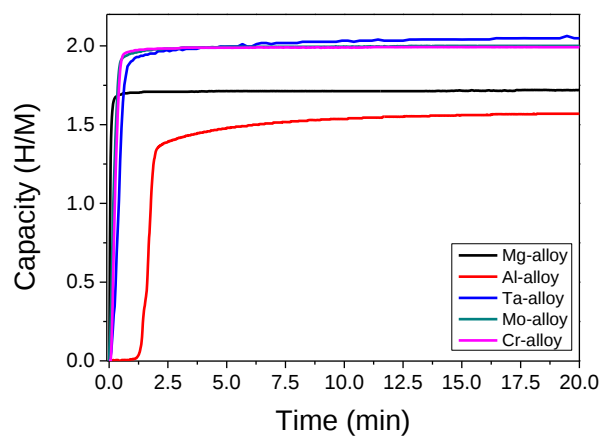


Figure SI-6: Attempts to correlate the *bcc* lattice parameters to the VEC and the average atomic radius.

