

Supplementary information

Uncovering the effect of Al addition on the hydrogen storage properties of the ternary TiVNb alloy

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Figure SI1. XRD patterns ($\lambda = 1.5406 \text{ \AA}$) and corresponding Rietveld refinement analysis for (a) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}$, (b) $\text{Al}_{0.175}(\text{TiVNb})_{0.825}$ and (c) $\text{Al}_{0.25}(\text{TiVNb})_{0.75}$

Figure SI2. Rietveld refinement analysis of the XRD pattern ($\lambda = 1.5406 \text{ \AA}$) for the full *fcc* dihydride $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.84}$.

Figure SI3. XRD pattern ($\lambda = 1.5406 \text{ \AA}$) for the *bcc* hydride of (a) $\text{Al}_{0.175}(\text{TiVNb})_{0.825}\text{H}_{0.81}$ and (b) $\text{Al}_{0.25}(\text{TiVNb})_{0.75}\text{H}_{0.69}$.

Figure SI4. Rietveld refinement analysis of the *ex situ* SR-XRD pattern ($\lambda = 0.72907 \text{ \AA}$) for the (a) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.8}$, (b) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.3}$, (c) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{0.9}$, (d) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{0.5}$ and (e) desorbed $\text{Al}_{0.05}(\text{TiVNb})_{0.95}$.

Figure SI5. Rietveld refinement analysis of the *ex situ* SR-XRD pattern ($\lambda = 0.72907 \text{ \AA}$) for the (a) $(\text{TiVNb})\text{H}_{2.0}$, (b) $(\text{TiVNb})\text{H}_{1.31}$, (c) $(\text{TiVNb})\text{H}_{0.9}$, (d) $(\text{TiVNb})\text{H}_{0.5}$ and (e) desorbed TiVNb.

Figure SI6. Rietveld refinement analysis of the XRD pattern ($\lambda = 1.5406 \text{ \AA}$) after TDS of (a) $\text{Al}_{0.175}(\text{TiVNb})_{0.825}$, (b) $\text{Al}_{0.10}(\text{TiVNb})_{0.90}$, (c) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}$, and (d) TiVNb.

Figure SI7. XRD pattern ($\lambda = 1.5406 \text{ \AA}$) after TDS of (a) $\text{Al}_{0.25}(\text{TiVNb})_{0.75}$.

Figure SI8. Rietveld refinement analysis of the *in situ* SR-XRD pattern during desorption ($\lambda = 0.67156 \text{ \AA}$) for the (a) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.84}$, (b) desorbed $\text{Al}_{0.05}(\text{TiVNb})_{0.95}$, (c) $(\text{TiVNb})\text{H}_{2.0}$, (d) desorbed TiVNb, everything at 25°C .

Figure SI9. Rietveld refinement analysis of the XRD pattern ($\lambda = 1.5406 \text{ \AA}$) for the hydride phase after cycling process of (a) $\text{Al}_{0.10}(\text{TiVNb})_{0.90}\text{H}_{1.50}$, (b) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.76}$, and (c) $(\text{TiVNb})\text{H}_{1.78}$.

Figure SI10. EDX-SEM chemical mapping of the hydride $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.76}$ after 10 cycles.

Table SI1. Lattice parameters of the $\text{Al}_x(\text{TiVNb})_{1-x}$ ($x=0$ [17], 0.05 , 0.10 [17], 0.175 , 0.25) desorbed samples after TDS.

Table SI2. Lattice parameters of the $\text{Al}_x(\text{TiVNb})_{1-x}$ ($x=0$, 0.05) alloys from *in situ* SR-XRD experiments.

Table SI3. EDX chemical analysis for $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.76}$ hydride after 10 cycles.

Figure S11. XRD patterns ($\lambda = 1.5406 \text{ \AA}$) and corresponding Rietveld refinement analysis for (a) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}$, (b) $\text{Al}_{0.175}(\text{TiVNb})_{0.825}$ and (c) $\text{Al}_{0.25}(\text{TiVNb})_{0.75}$.

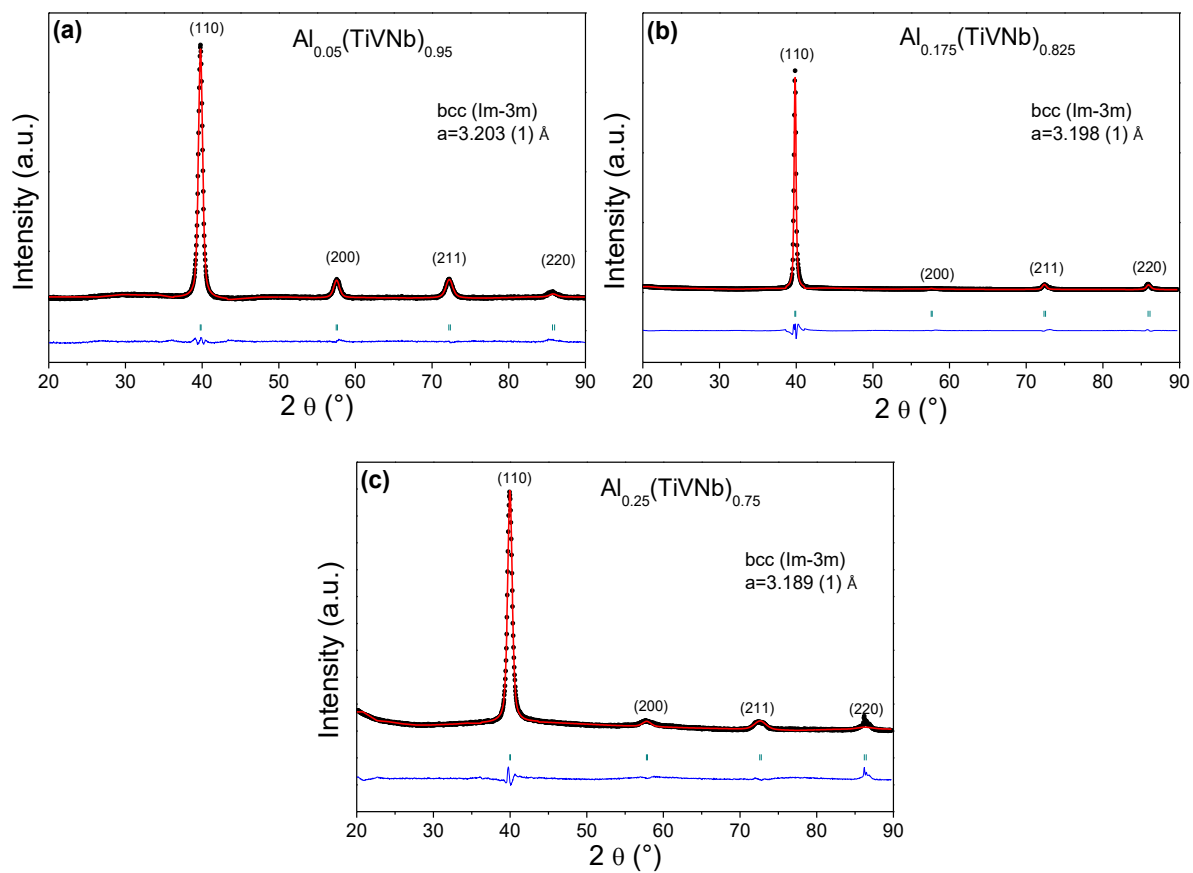


Figure	Composition	<i>with all non-excluded points</i>			Bragg R-factor
		Rp	Rwp	Chi ²	
S11a	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}$	11.5	6.13	3	1.18
S11b	$\text{Al}_{0.175}(\text{TiVNb})_{0.825}$	15.8	14.5	88	1.78
S11c	$\text{Al}_{0.25}(\text{TiVNb})_{0.75}$	21.9	11.8	11.5	3.47

Figure SI2. Rietveld refinement analysis of the XRD pattern ($\lambda = 1.5406\text{\AA}$) for the full *fcc* dihydride $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.84}$.

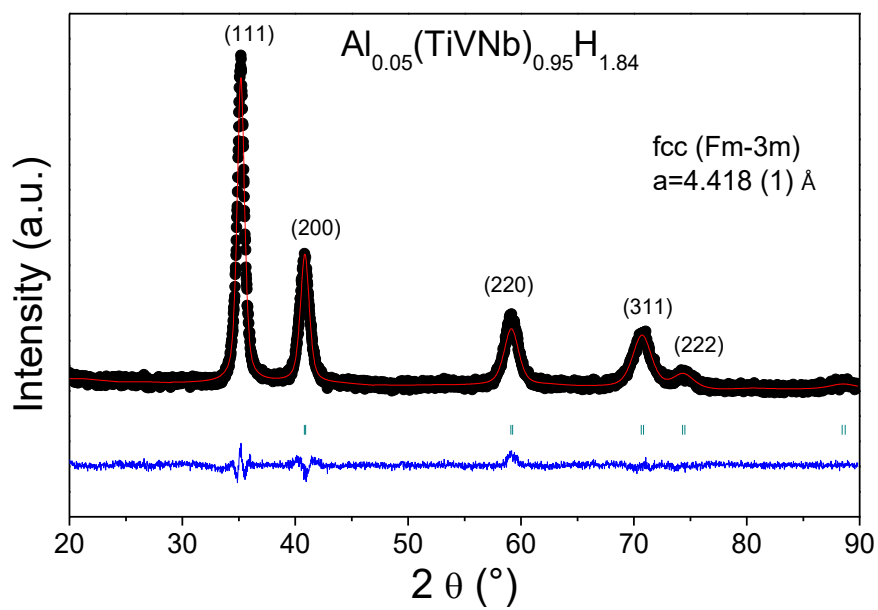
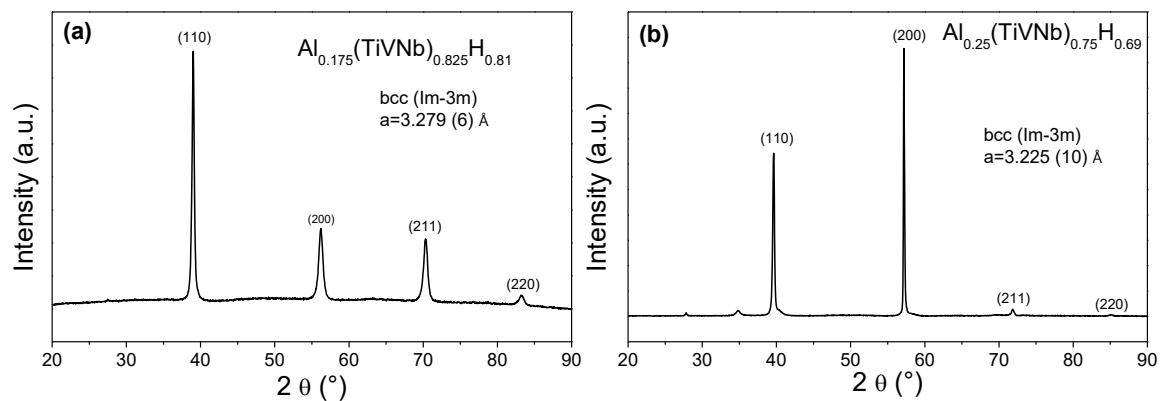


Figure	Composition	with all non-excluded points			Bragg R-factor
		Rp	Rwp	Chi ²	
SI2	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.84}$	18.2	15.1	1.52	2.01

Figure SI3. XRD pattern ($\lambda = 1.5406\text{\AA}$) for the *bcc* hydride of (a) $\text{Al}_{0.175}(\text{TiVNb})_{0.825}\text{H}_{0.81}$ and (b) $\text{Al}_{0.25}(\text{TiVNb})_{0.75}\text{H}_{0.69}$.



Lattice parameter obtained by CELREF unit cell refinement of powder diffraction data software (<http://ccp14.cryst.bbk.ac.uk/solution/unitcellrefine/index.html>).

Figure S14. Rietveld refinement analysis of the *ex situ* SR-XRD pattern ($\lambda = 0.72907 \text{ \AA}$) for the (a) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.8}$, (b) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.3}$, (c) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{0.9}$, (d) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{0.5}$ and (e) desorbed $\text{Al}_{0.05}(\text{TiVNb})_{0.95}$.

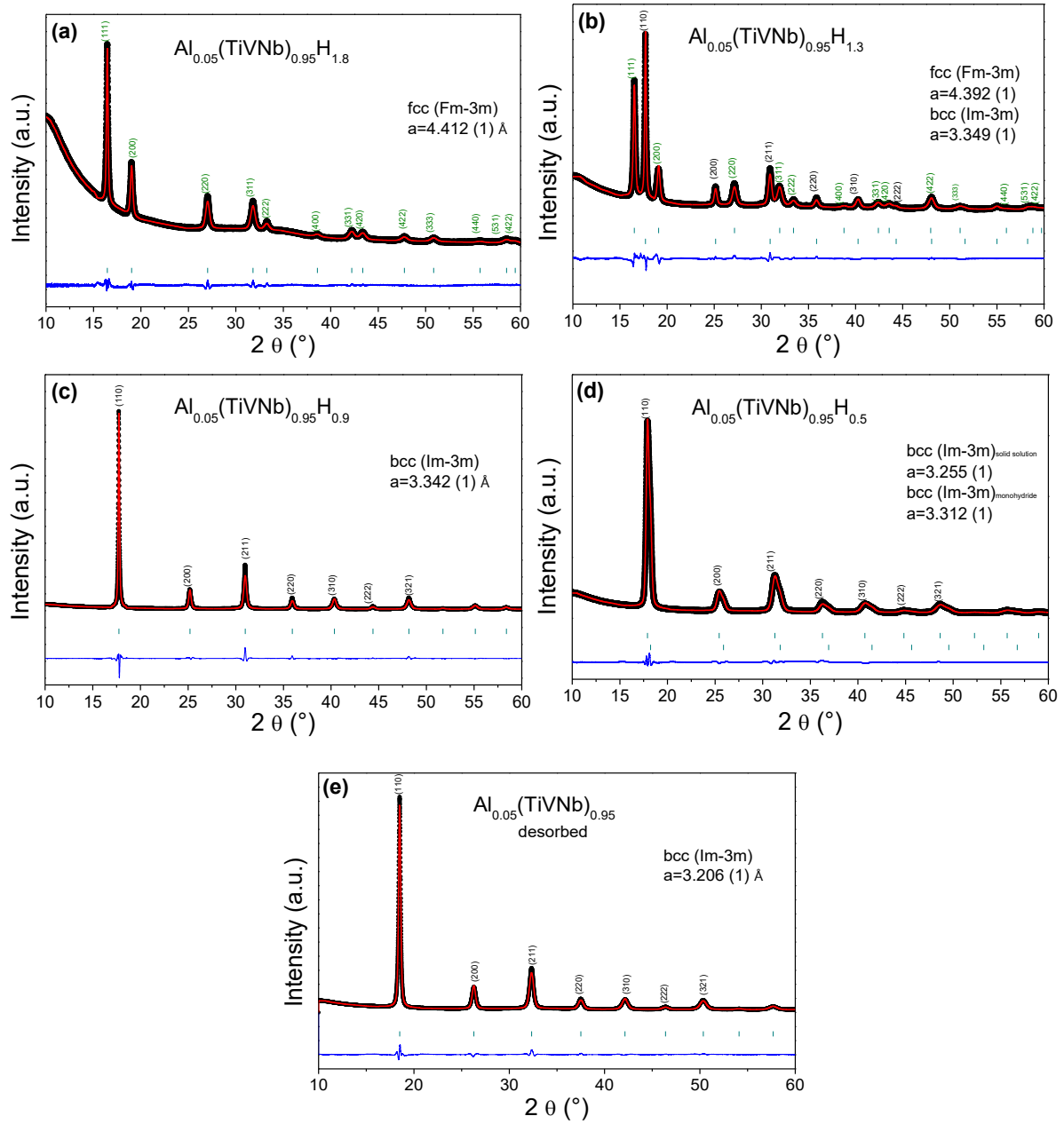


Figure	Composition	with all non-excluded points			Bragg R-factor
		Rp	Rwp	Chi ²	
S14a	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.8}$	25.4	15.9	3.47	6.94
S14b	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.3}$	11.8	12.0	12.9	3.40 fcc 3.48 bcc
S14c	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{0.9}$	12.0	15.0	33.7	4.45
S14d	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{0.5}$	8.83	10.8	14.9	4.51 bcc monohydride 5.42 bcc solid solution
S14e	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}$ desorbed	8.66	10.6	16.3	1.53

Figure SI5. Rietveld refinement analysis of the *ex situ* SR-XRD pattern ($\lambda = 0.72907 \text{ \AA}$) for the (a) $(\text{TiVNb})\text{H}_{2.0}$, (b) $(\text{TiVNb})\text{H}_{1.31}$, (c) $(\text{TiVNb})\text{H}_{0.9}$, (d) $(\text{TiVNb})\text{H}_{0.5}$ and (e) desorbed TiVNb.

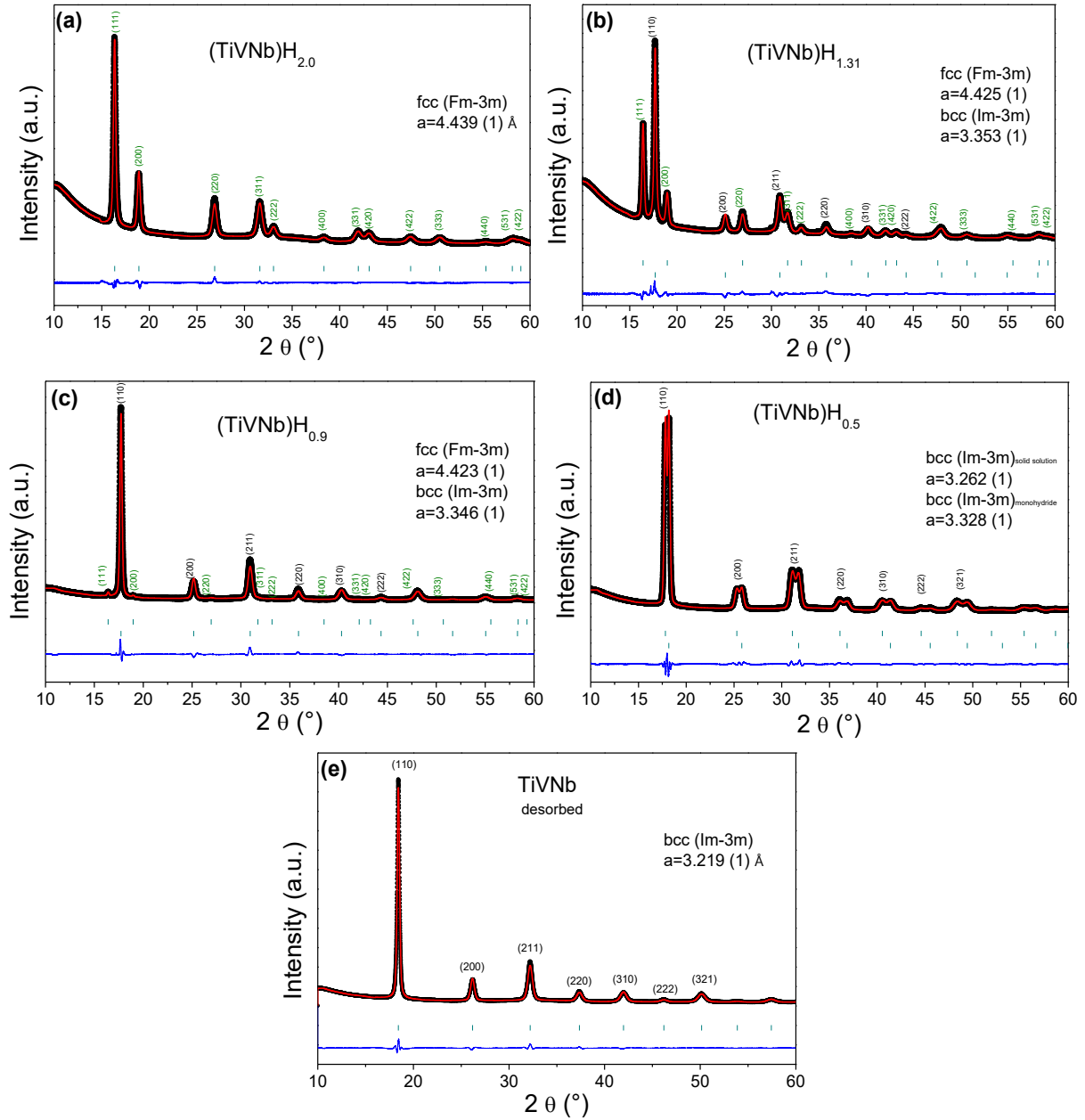


Figure	Composition	with all non-excluded points			Bragg R-factor
		Rp	Rwp	Chi ²	
SI5a	$(\text{TiVNb})\text{H}_{2.0}$	8.96	8.18	3.94	3.22
SI5b	$(\text{TiVNb})\text{H}_{1.31}$	12.5	12.9	9.87	4.66 fcc 6.50 bcc
SI5c	$(\text{TiVNb})\text{H}_{0.9}$	12.4	14.2	24.1	31.6 fcc 4.91 bcc
SI5d	$(\text{TiVNb})\text{H}_{0.5}$	7.24	8.08	9.15	2.67 bcc monohydride 2.94 bcc solid solution
SI5e	TiVNb desorbed	7.91	9.64	11.2	2.05

Figure SI6. Rietveld refinement analysis of the XRD pattern ($\lambda = 1.5406 \text{ \AA}$) after TDS of (a) $\text{Al}_{0.175}(\text{TiVNb})_{0.825}$, (b) $\text{Al}_{0.10}(\text{TiVNb})_{0.90}$, (c) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}$, and (d) TiVNb.

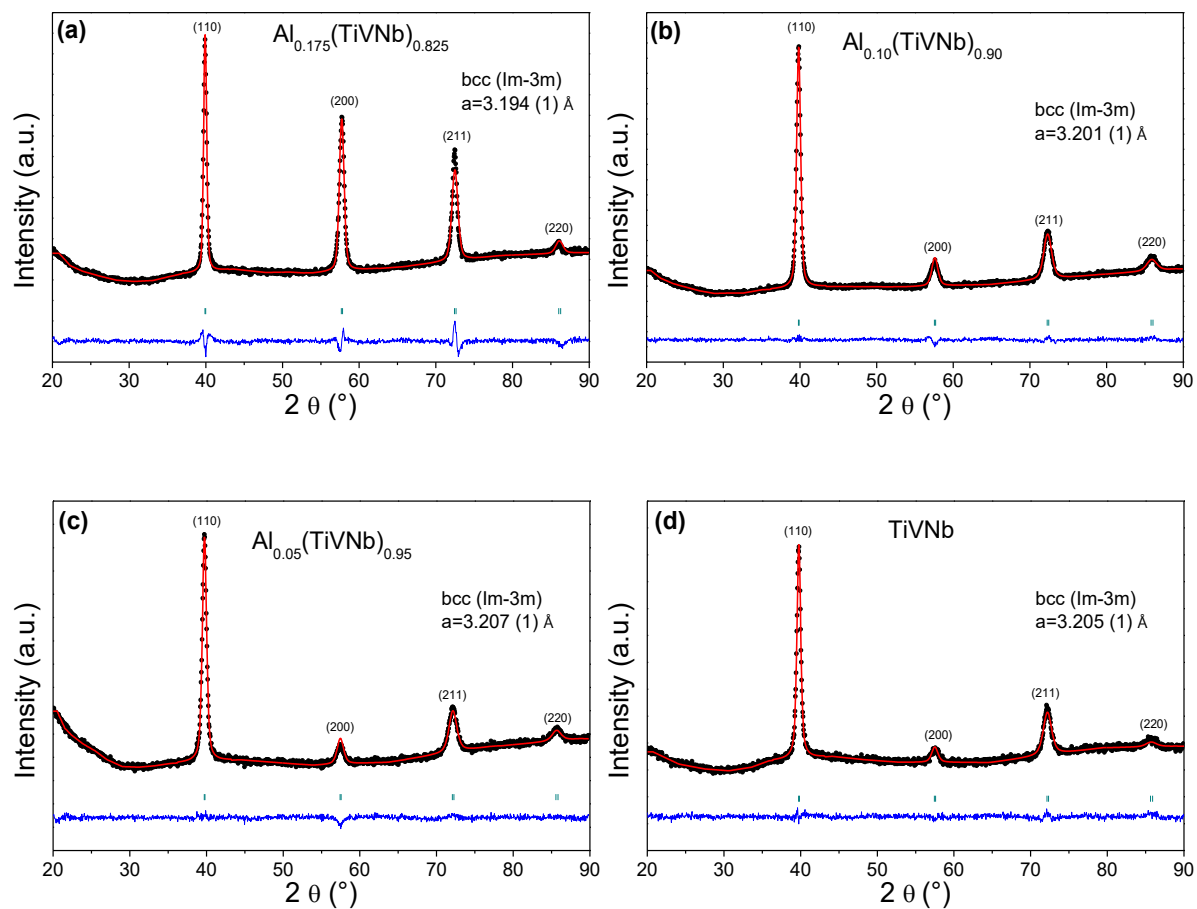


Figure	Composition	with all non-excluded points			Bragg R-factor
		Rp	Rwp	Chi ²	
SI6a	$\text{Al}_{0.175}(\text{TiVNb})_{0.825}$	26.5	13.9	2.67	1.98
SI6b	$\text{Al}_{0.10}(\text{TiVNb})_{0.90}$	21.8	10.4	1.50	1.87
SI6c	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}$	31.3	13.8	1.44	1.53
SI6d	TiVNb	37.1	15.1	1.28	2.38

Figure SI7. XRD pattern ($\lambda = 1.5406\text{\AA}$) after TDS of (a) $\text{Al}_{0.25}(\text{TiVNb})_{0.75}$.

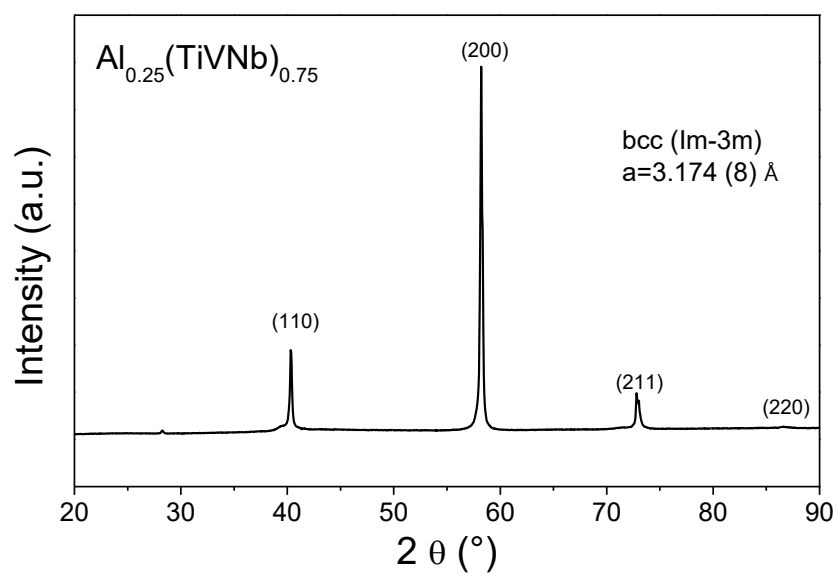


Figure SI8. Rietveld refinement analysis of the *in situ* SR-XRD pattern during desorption ($\lambda = 0.67156 \text{ \AA}$) for the (a) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.84}$, (b) desorbed $\text{Al}_{0.05}(\text{TiVNb})_{0.95}$, (c) $(\text{TiVNb})\text{H}_{2.0}$, (d) desorbed TiVNb at 25°C .

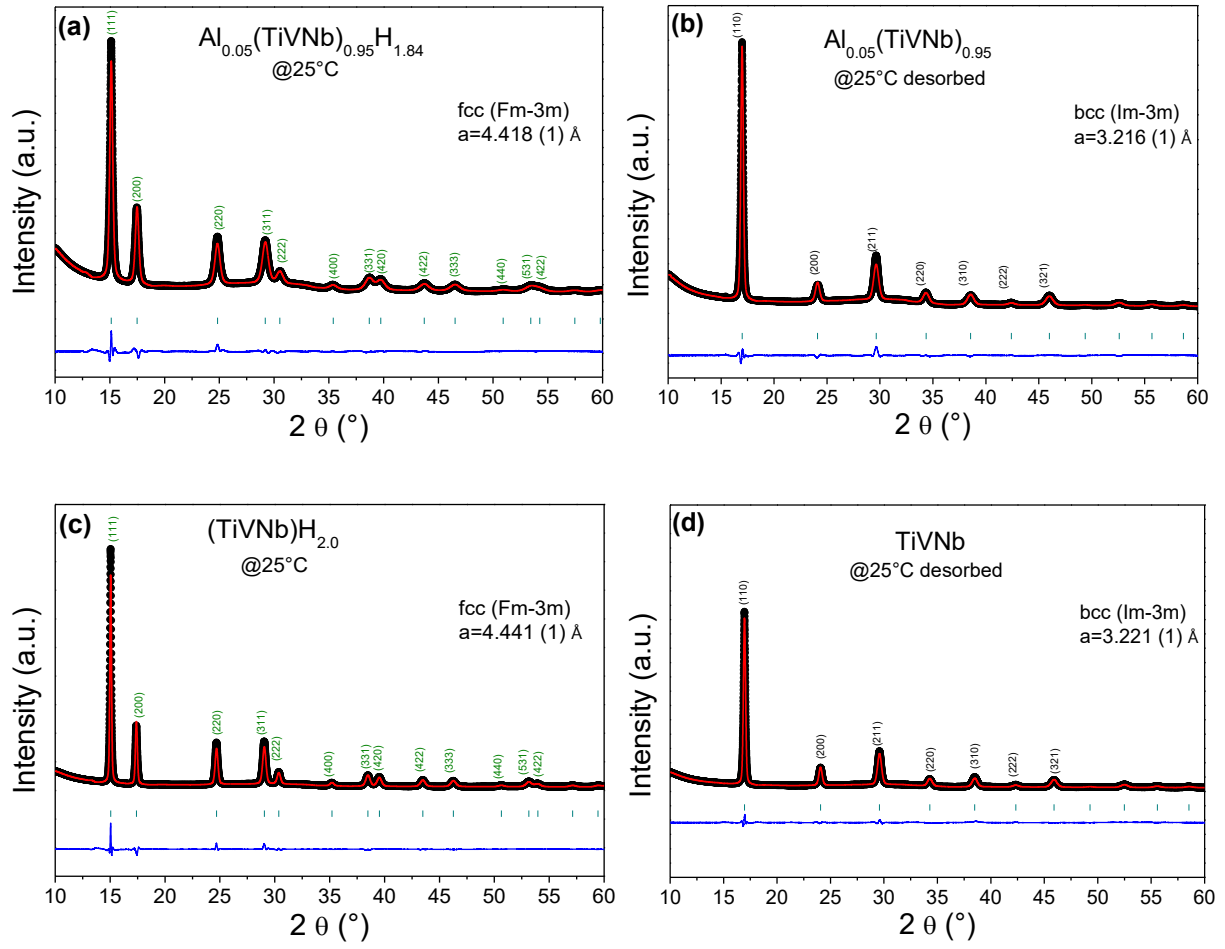


Figure	Composition	with all non-excluded points			Bragg R-factor
		Rp	Rwp	χ^2	
SI8a	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.84}$	9.73	10.6	15.6	3.69
SI8b	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}$	10.5	12.2	13.9	4.18
SI8c	$(\text{TiVNb})\text{H}_{2.0}$	10.6	11.8	21.8	5.79
SI8d	TiVNb	9.07	11.0	13.2	4.46

Figure SI9. Rietveld refinement analysis of the XRD pattern ($\lambda = 1.5406\text{\AA}$) for the hydride phase after cycling process of (a) $\text{Al}_{0.10}(\text{TiVNb})_{0.90}\text{H}_{1.50}$, (b) $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.76}$, and (c) $(\text{TiVNb})\text{H}_{1.78}$.

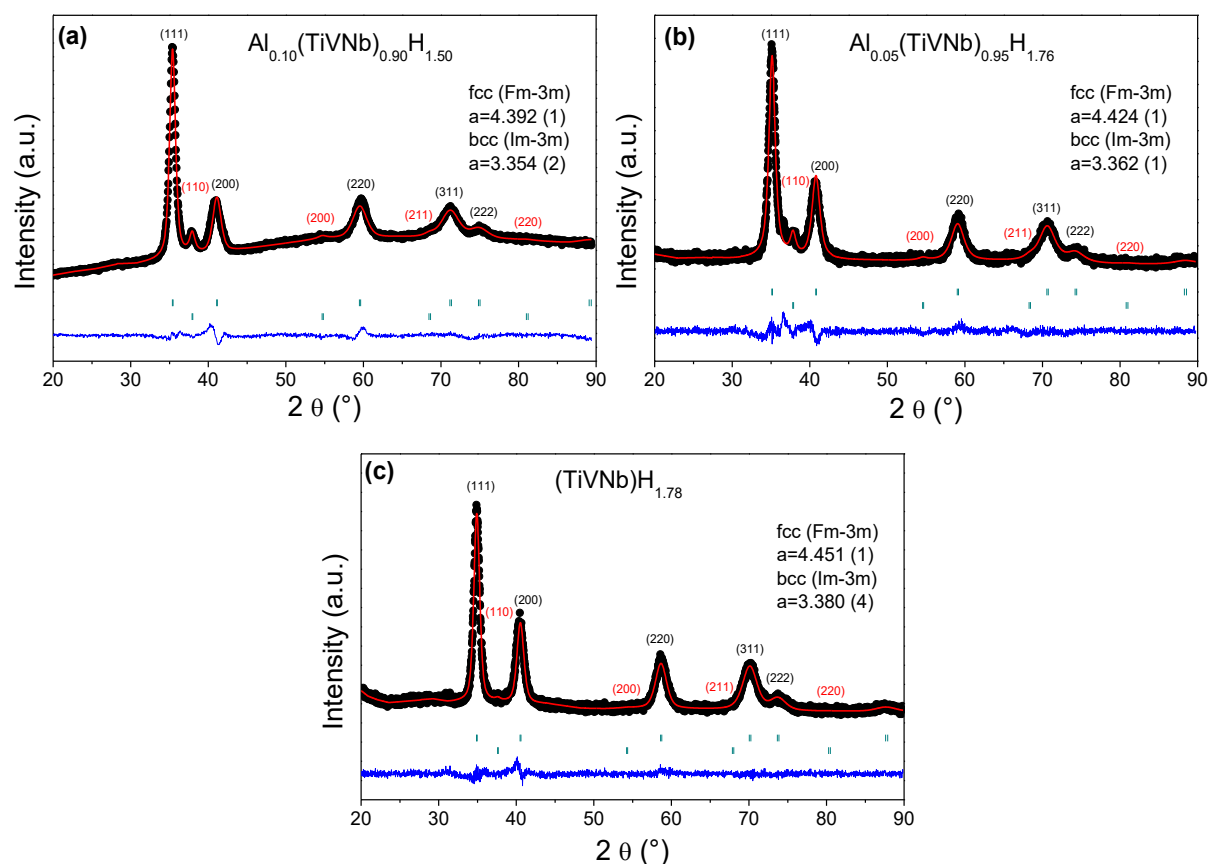


Figure	Composition	<i>with all non-excluded points</i>			Bragg R-factor
		Rp	Rwp	Chi ²	
SI9a	$\text{Al}_{0.10}(\text{TiVNb})_{0.90}\text{H}_{1.50}$	16.3	12.1	3.40	2.53 fcc 6.98 bcc
SI9b	$\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.76}$	20.9	18.1	1.84	1.93 fcc 9.00 bcc
SI9c	$(\text{TiVNb})\text{H}_{1.78}$	21.1	15.9	1.35	2.97 fcc 6.59 bcc

Figure SI10. EDX-SEM chemical mapping of the hydride $\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.76}$ after 10 cycles.

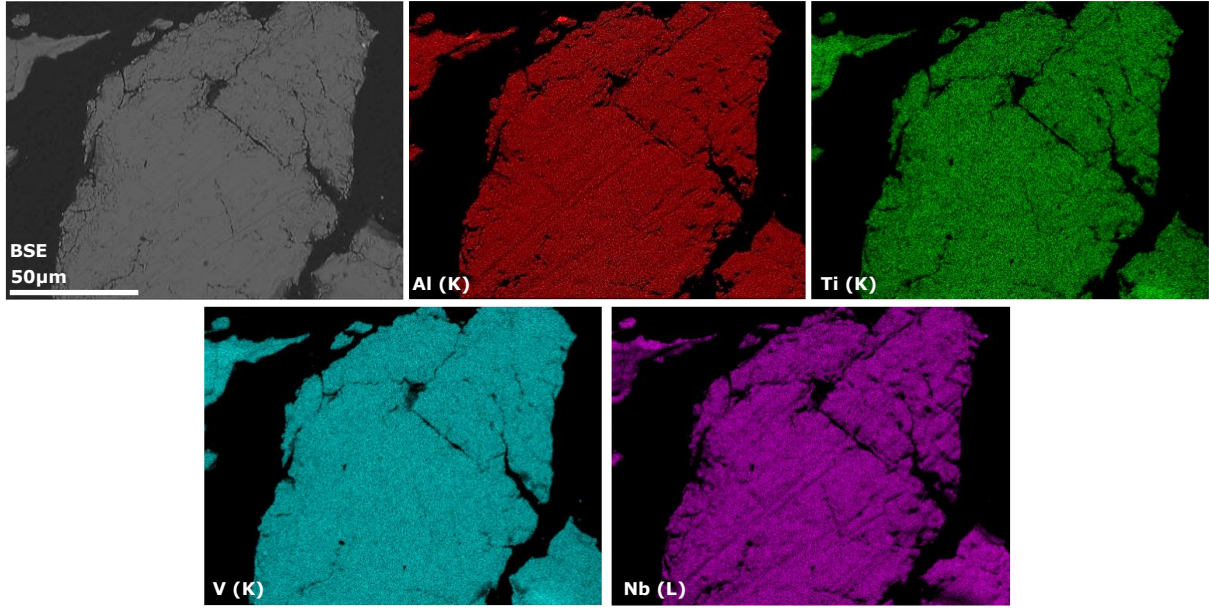


Table SI1. Lattice parameters of the $\text{Al}_x(\text{TiVNb})_{1-x}$ ($x=0$ [17], 0.05, 0.10 [17], 0.175, 0.25) desorbed samples after TDS.

Composition	Phase structure	Lattice parameter (Å)
$\text{Al}_{0.25}(\text{TiVNb})_{0.75}$	<i>bcc</i>	3.174 (8) *
$\text{Al}_{0.175}(\text{TiVNb})_{0.825}$	<i>bcc</i>	3.194(1)
$\text{Al}_{0.10}(\text{TiVNb})_{0.90}$	<i>bcc</i>	3.201(1)
$\text{Al}_{0.05}(\text{TiVNb})_{0.95}$	<i>bcc</i>	3.207(1)
TiVNb	<i>bcc</i>	3.205(1)

*Obtained by CELREF.

Table SI2. Lattice parameters of the $\text{Al}_x(\text{TiVNb})_{1-x}$ ($x=0, 0.05$) alloys from *in situ* SR-XRD experiments.

Composition	Form	Phase structure	Phase fraction (%)	Lattice parameter (Å)	Temperature (°C)
$\text{Al}_{0.05}(\text{TiVNb})_{0.95}\text{H}_{1.84}$	dihydride	<i>fcc</i>	100	4.418(1)	25
		<i>fcc</i>	100	4.421 (1)	152.3
		<i>bcc_{mh}**</i>	3.59	3.350 (1)	166
		<i>fcc</i>	96.41	4.421 (1)	
		<i>bcc_{mh}**</i>	7.03	3.348 (1)	188.7
		<i>fcc</i>	92.97	4.421 (1)	
		<i>bcc_{mh}**</i>	13.70	3.344 (1)	252
		<i>fcc</i>	86.30	4.418(1)	
		<i>bcc_{mh}**</i>	60.57	3.318(1)	315.4
		<i>fcc</i>	39.43	4.404(1)	
		<i>bcc</i>	100	3.282(1)	347
		<i>bcc</i>	100	3.229(1)	450.1
$\text{Al}_{0.05}(\text{TiVNb})_{0.95}$	desorbed	<i>bcc</i>	100	3.216(1)	25

(TiVNb)H _{2.0}	dihydride	<i>fcc</i>	100	4.441(1)	25
TiVNb		<i>fcc</i>	100	4.445(1)	180.1
		<i>fcc</i>	100	4.445 (1)	251.9
		<i>bcc_{mh}**</i>	0.83	3.364(1)	301.2
		<i>fcc</i>	99.17	4.442(1)	
		<i>bcc_{mh}**</i>	44.73	3.318(1)	332.7
		<i>fcc</i>	55.27	4.439(1)	
		<i>bcc_{mh}**</i>	85.67	3.308(1)	337.2
		<i>fcc</i>	14.33	4.438(1)	
		<i>bcc</i>	100	3.270(1)	355.1
		<i>bcc</i>	100	3.234(1)	449.6
TiVNb	desorbed	<i>bcc</i>	100	3.221(1)	25

* *bcc_{ss}*= *bcc solid solution* ** *bcc_{mh}*=*bcc monohydride*

Table SI3. EDX chemical analysis for Al_{0.05}(TiVNb)_{0.95}H_{1.76} hydride after 10 cycles.

Composition	Element	Nominal (at. %)	Overall average (at. %)	Nb rich region (at. %)	Nb poor region (at. %)
Al _{0.05} (TiVNb) _{0.95}	Al (K)	5	4.61 (0.22)	4.63 (0.22)	4.62 (0.21)
	Ti (K)	31.6	31.58 (0.93)	31.11(0.77)	32.38(0.66)
	V (K)	31.6	31.48 (0.97)	30.96(0.79)	32.44(0.51)
	Nb (L)	31.6	32.32 (1.74)	33.30 (1.28)	30.55(1.08)