

# SUPPLEMENTARY MATERIAL

## Fabrication of Biomedical Ti-Zr-Nb by Reducing Metal Oxides with Calcium Hydride

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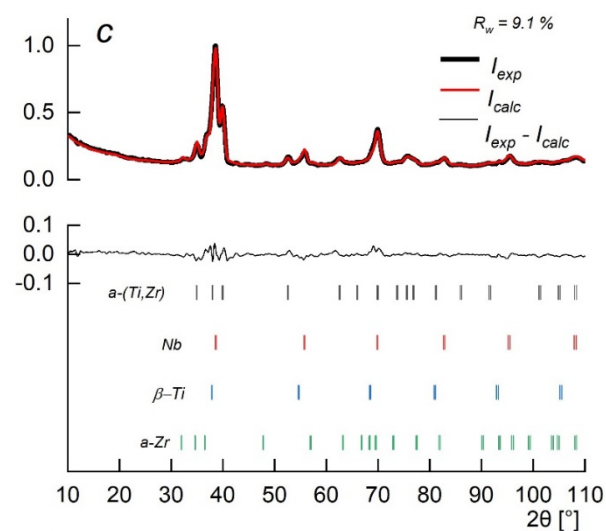
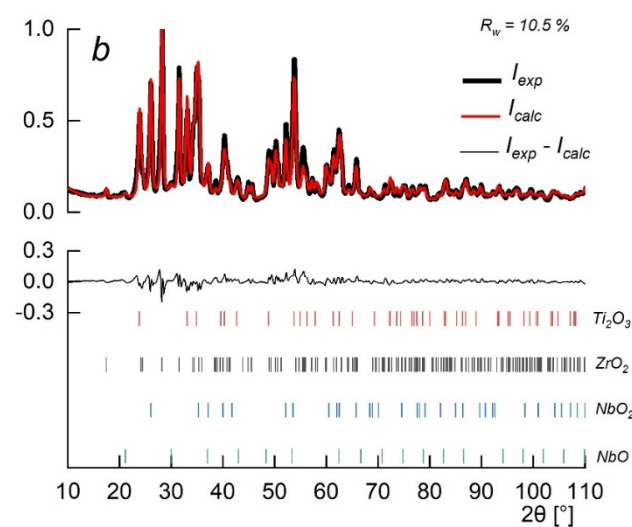
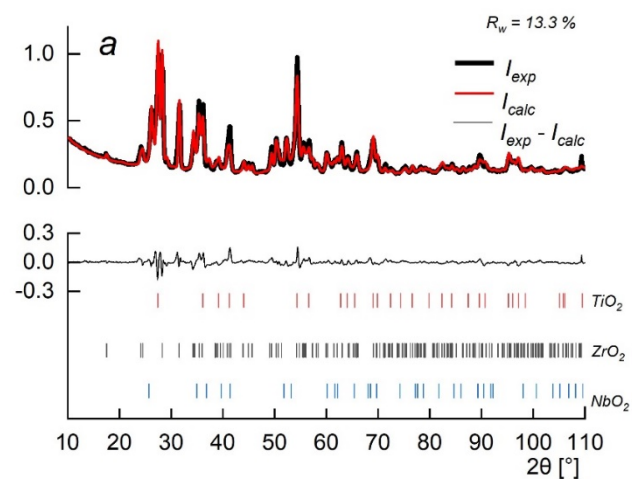
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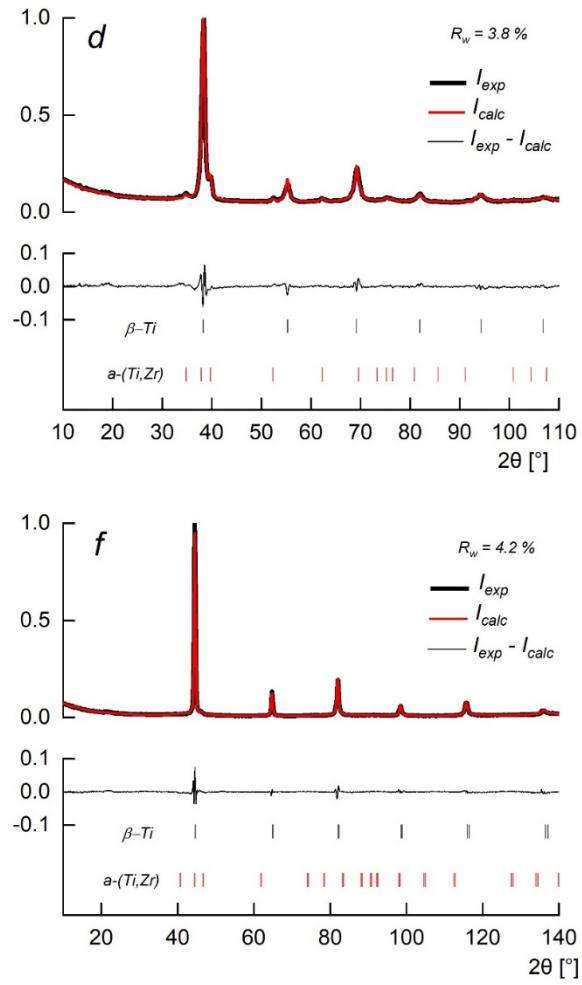
**Table S1.** Design matrix.

Temperature, °C	Exposure, h	$\beta$ -Ti, % vol.	Pressing method*
900	0.0	0.0	0
900	2.0	0.0	0
900	4.0	0.0	0
900	6.0	0.0	0
900	8.0	0.0	0
1000	4.0	10.9	0
1000	6.0	10.3	0
1050	4.0	53.8	0
1050	6.0	50.5	0
1100	0.5	55.2	0
1100	1.0	59.8	0
1100	2.0	70.2	0
1100	4.0	72.2	0
1100	6.0	70.7	0
1150	4.0	56.3	0
1150	6.0	59.4	0
1200	0.0	62.7	0
1200	2.0	69.7	0
1200	4.0	75.7	0
1200	6.0	79.4	0
1200	10.0	84.2	0
1200	12.0	93.2	0
1100	0.5	55.2	0
1100	1.0	59.8	0
1100	2.0	70.2	0
1150	4.0	56.3	0
1150	6.0	59.4	0
1200	10.0	84.2	0
1200	12.0	93.2	0
1000	4.0	13.7	1
1000	6.0	29.2	1
1050	4.0	62.2	1
1050	6.0	55.4	1
1100	1.0	57.4	1
1100	2.0	67.5	1
1100	4.0	65.3	1
1100	6.0	67.8	1
1150	4.0	59.9	1
1150	6.0	62.7	1
1200	0.0	58.4	1
1200	2.0	75.7	1
1200	4.0	78.0	1
1200	6.0	83.0	1
1000	0.0	2.9	1

\* – 0 – hand pressing of the charge; 1 – hydraulic pressing of the charge under 56 MPa

The pressing predictor, which is a categorical variable, is varied from 0 to 1, where 0 means a low load of 0.7 MPa and 1 means a high load under 56 MPa.





**Figure S1.** Experimental and calculated XRD patterns of calcium-hydride powders synthesized at various temperatures and exposure: *a* – 900 °C, 0 h; *b* – 1000 °C, 0 h; *c* – 1000 °C, 6 h; *d* – 1200, 4 h; *f* – 1200, 12 h. *a*, *c*, *d*, *f* - ( $\rho_{\text{charge}} = 1.4 \text{ g/cm}^3$ ); *b* - ( $\rho_{\text{charge}} = 1.6 \text{ g/cm}^3$ ).  $R_w$  – weighted average Bragg *R*-factor.

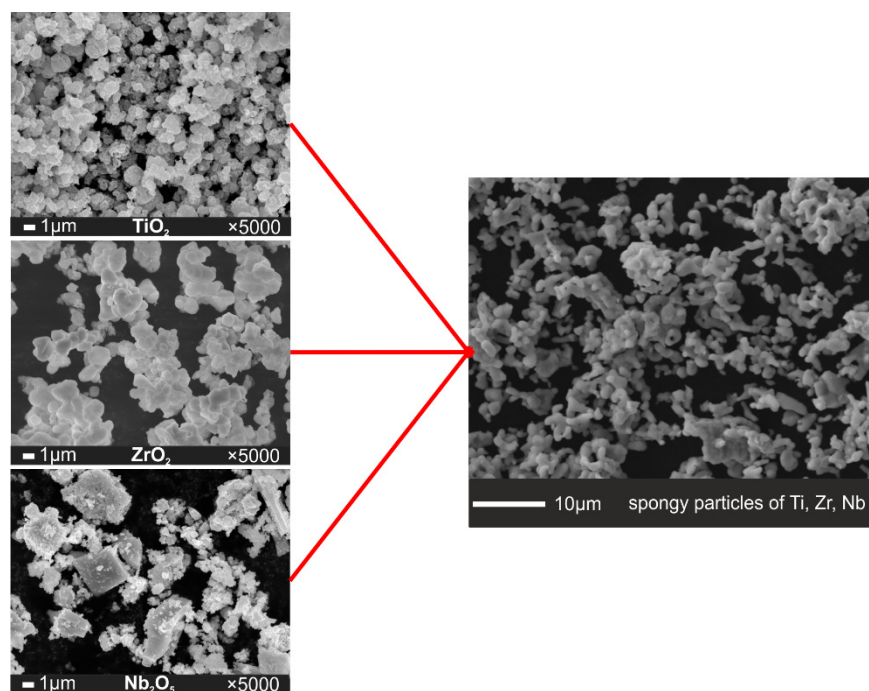
**Table S2.** Several structural parameters of the phases, which Bragg positions are shown in Figure S1.

Figure S1.

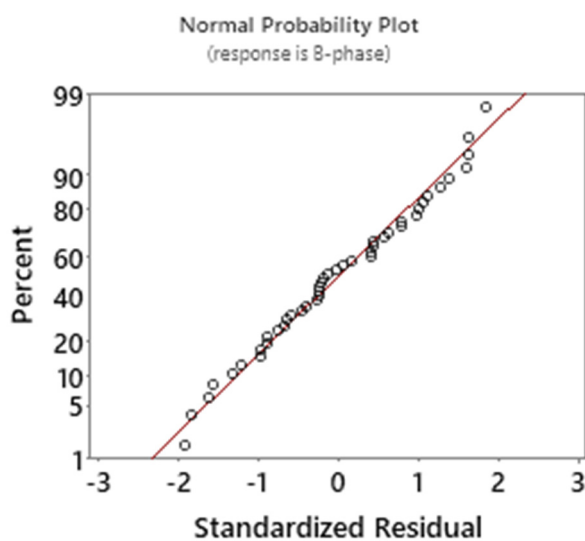
Phase	Structure type (s.g.)	Lattice parameters	Phase content	
			Weight fraction, %	Volume fraction, %
Graph a)				
TiO <sub>2</sub>	P 42/m n m (136)	a= 4.597 c= 2.961	65.7	72.2
ZrO <sub>2</sub>	P 1 21/c 1 (14)	a= 5.138 b= 5.200 c= 5.309 β=99.226	25.4	20.7
NbO <sub>2</sub>	P 42/m n m (136)	a= 4.838 c= 2.990	8.9	7.1
Graph b)				
ZrO <sub>2</sub>	P 1 21/c 1 (14)	a= 5.140 b= 5.199 c= 5.310 β =99.196	31.5	27.8
Ti <sub>2</sub> O <sub>3</sub>	R -3 c (167)	a= 5.145 c= 13.655	53.3	59.2
NbO <sub>2</sub>	P 42/m n m (136)	a= 4.838 c= 2.990	13.2	11.5
NbO	P m -3 m (221)	a= 4.207	2.1	1.5
Graph c)				
β-Ti	I m -3 m (229)	a= 3.345	11.3	10.3
Nb	I m -3 m (229)	a= 3.296	24.4	17.9
α-Zr	P 63/m m c (194)	a= 3.201 c= 5.133	7.8	7.6
α-(Ti,Zr)	P 63/m m c (194)	a= 2.966 c= 4.742	56.5	64.2
Graph d)				
β-Ti	I m -3 m (229)	a= 3.325	80.6	75.7
α-(Ti,Zr)	P 63/m m c (194)	a= 2.981 c= 4.754	19.4	24.6
Graph f)				
β-Ti	I m -3 m (229)	a= 3.343	94.9	93.2
α-(Ti,Zr)	P 63/m m c (194)	a= 2.978 c= 4.837	5.1	5.4

\* The solid solution of Zr and Nb in Ti lattice is referred as  $\beta$ -Ti in the table and in the corresponding Figure S2;  $\alpha$ -(Ti,Zr) indicates that there is the difference between a calculated lattice parameter and the parameter of pure  $\alpha$ -Ti.

The calcium-hydride powders of Ti, Zr, and Nb possess a spongy-type morphology regardless of the morphology of initial oxides ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{Nb}_2\text{O}_5$ ) (Figure S2).



**Figure S2.** Typical morphology of Ti, Zr, and Nb reduced by calcium hydride.



**Figure S3.** Normal probability plot of standardized residuals for the elaborated model.