

# Supplemental Information

## Tailoring of TiAl6V4 Surface Nanostructure for Enhanced *in-vitro* Osteoblast Response via Gas/Solid (Non-Line-of-Sight) Oxidation/Reduction Reactions

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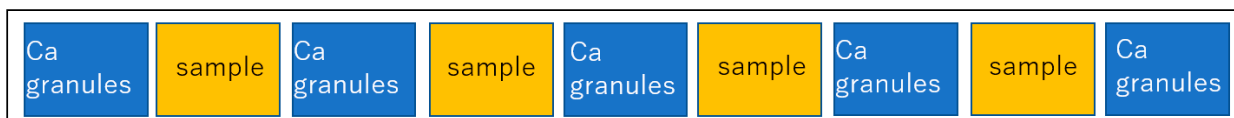
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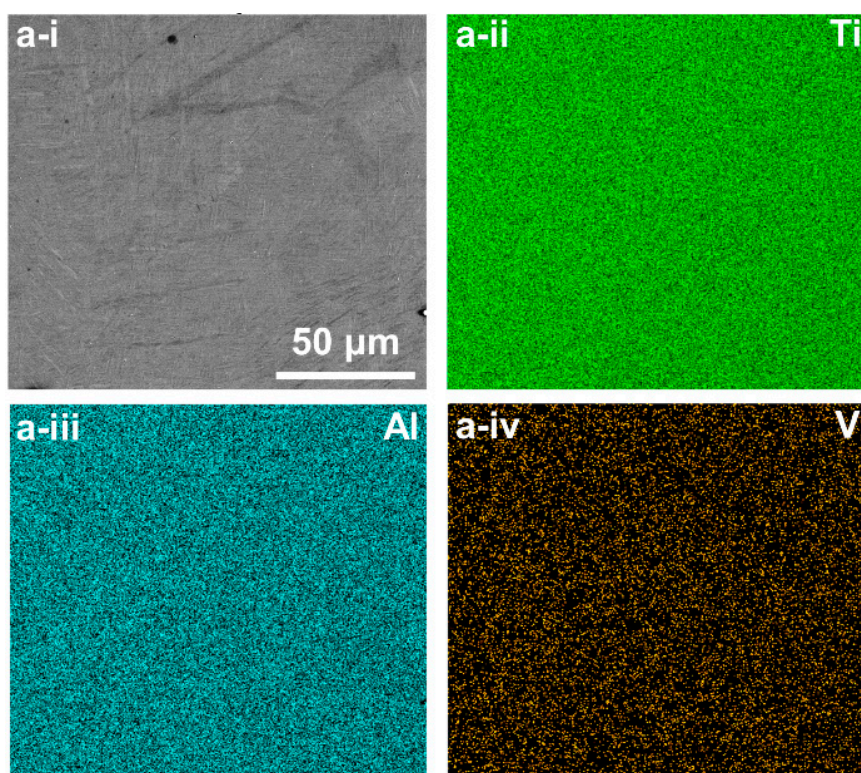
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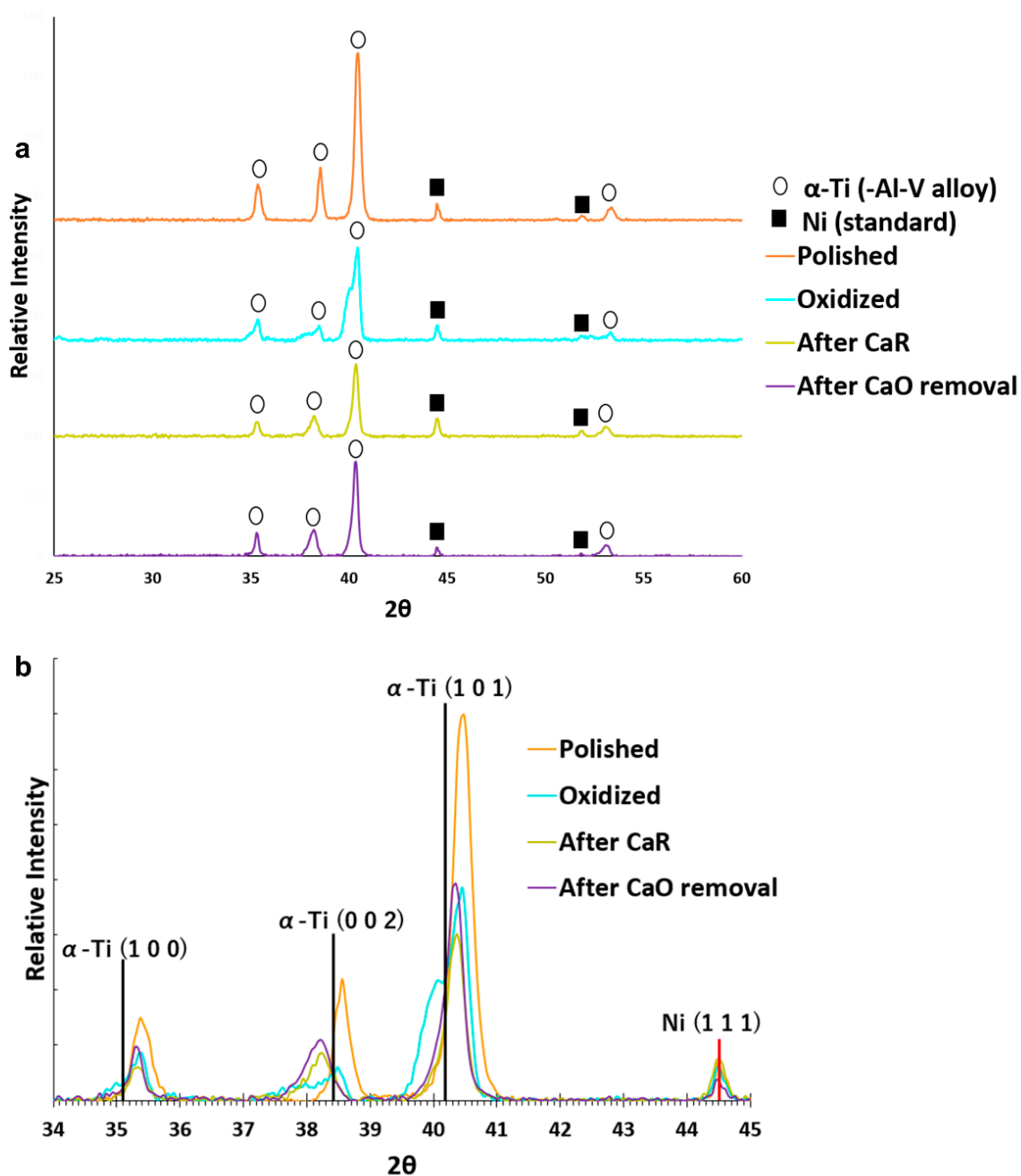
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**Supplemental Figure S1.** Schematic illustration of the alternating arrangement of oxidized TiAl6V4 specimens (in Ti crucibles) with Ca granules (also in Ti crucibles), all of which were sealed within a steel ampoule, for the calciothermic reaction step.

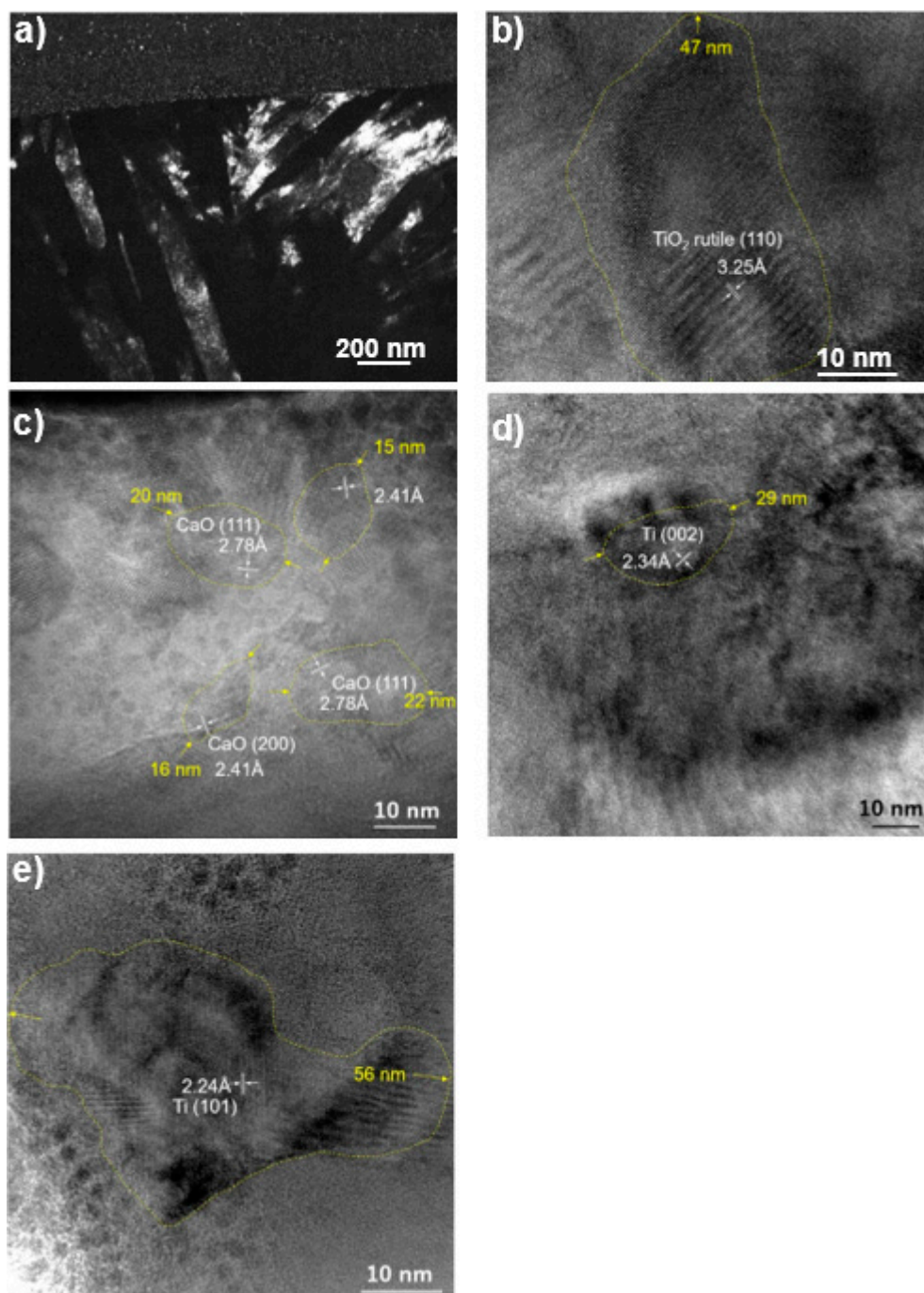


**Supplemental Figure S2.** Characterization of a starting polished DMLS TiAl6V4 specimen: (a-i) top-down BSE (backscattered electron) image of the surface and associated EDX elemental maps for (a-ii) titanium, (a-iii) aluminum, and (a-iv) vanadium.

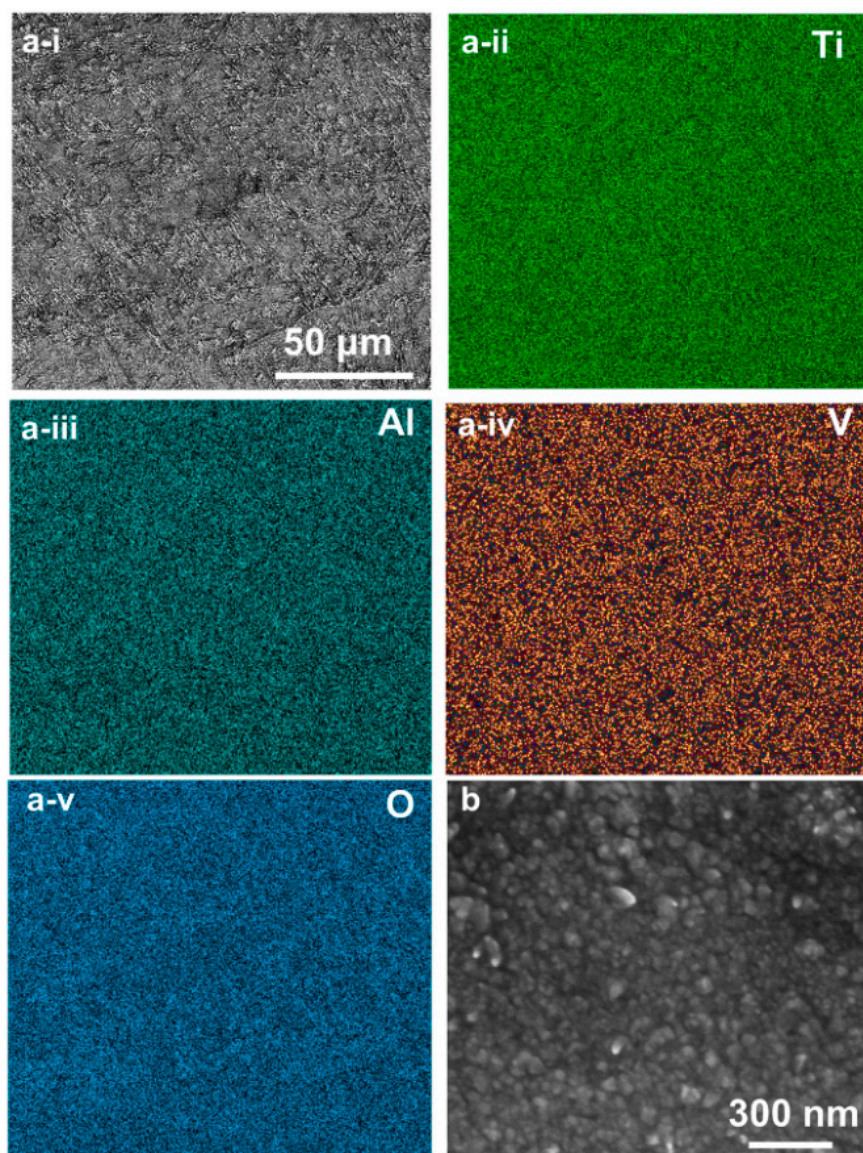


**Supplemental Figure S3.** XRD analyses of polished DMLS TiAl6V4 specimen surfaces after each reaction stage: (a) separated XRD patterns ( $2\theta = 25$ -60 degrees); (b) superimposed XRD patterns ( $2\theta = 34$ -45 degrees), with vertical black lines indicating the positions of diffraction peaks for pure  $\alpha$ -titanium (note: “After CaR” indicates after the calciothermic reaction).



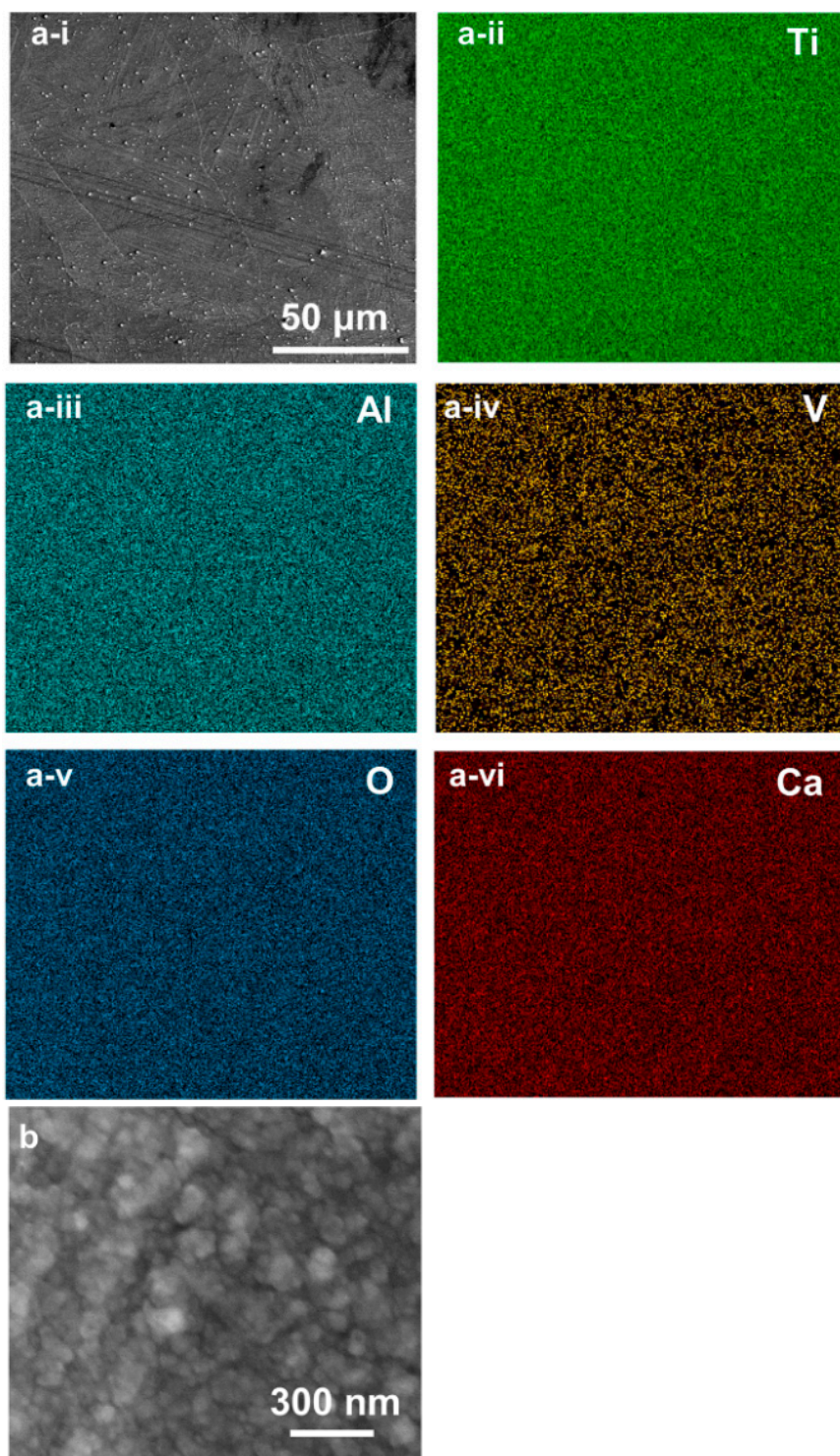


**Supplemental Figure S4.** TEM analyses at various stages of reaction of polished DMLS TiAl6V4 specimens: (a) Dark field TEM image of an ion-milled cross-section of the polished starting DMLS specimen revealing  $\alpha$ -TiAl6V4 crystals; (b) HRTEM image of the nanocrystalline rutile TiO<sub>2</sub> layer generated upon oxidation at 600 °C for 6 h in air; (c) HRTEM image of the nanocrystalline CaO layer formed upon reaction of the oxidized TiAl6V4 specimen with Ca(g) at 700 °C for 1 h; (d) HRTEM image of the nanocrystalline  $\alpha$ -Ti-rich layer formed upon reaction of the oxidized TiAl6V4 specimen with Ca(g) at 700 °C for 1 h; (e) HRTEM image of the nanocrystalline  $\alpha$ -Ti-rich layer after selective acetic acid dissolution of the CaO generated upon reaction of the oxidized TiAl6V4 specimen with Ca(g) at 700 °C for 1 h.

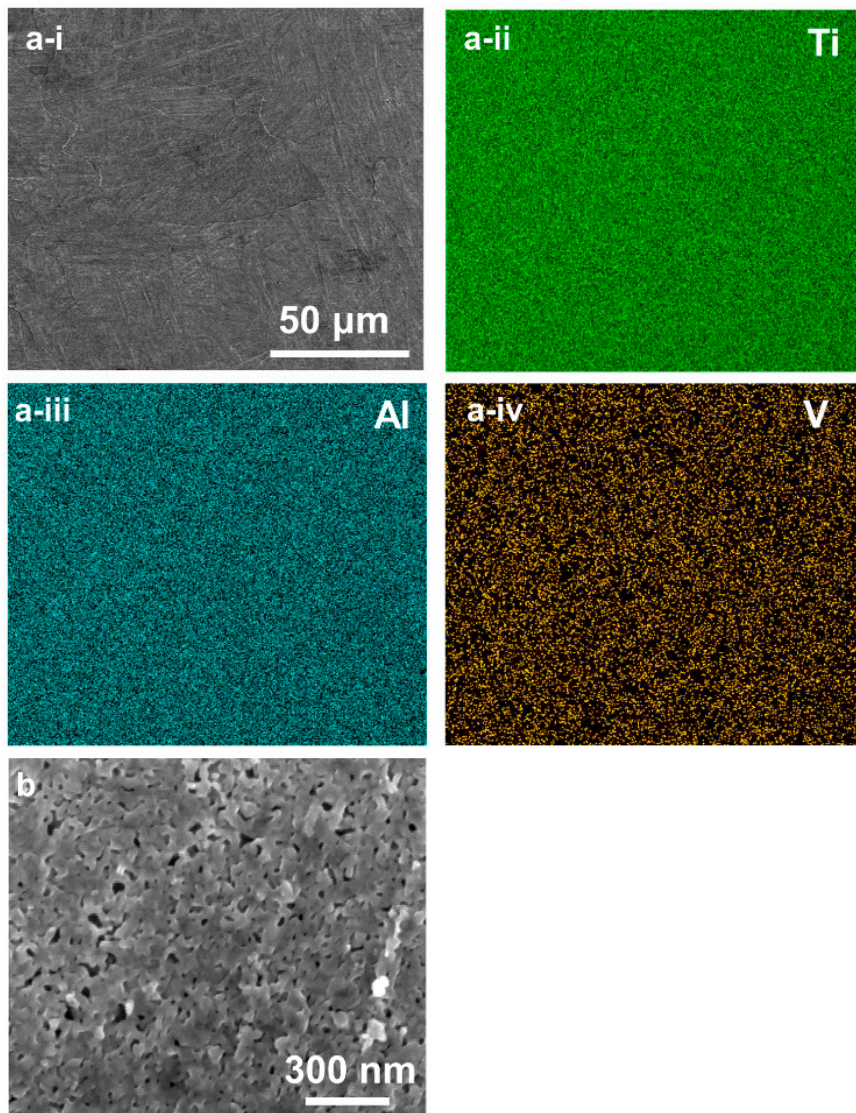


**Supplemental Figure S5.** Characterization of a polished DMLS TiAl6V4 specimen after exposure to air at 600°C for 6 h: **(a-i)** top-down BSE image of the surface and associated EDX elemental maps for **(a-ii)** titanium, **(a-iii)** aluminum, **(a-iv)** vanadium, and **(a-v)** oxygen; **(b)** higher-magnification top-down SE image of the surface



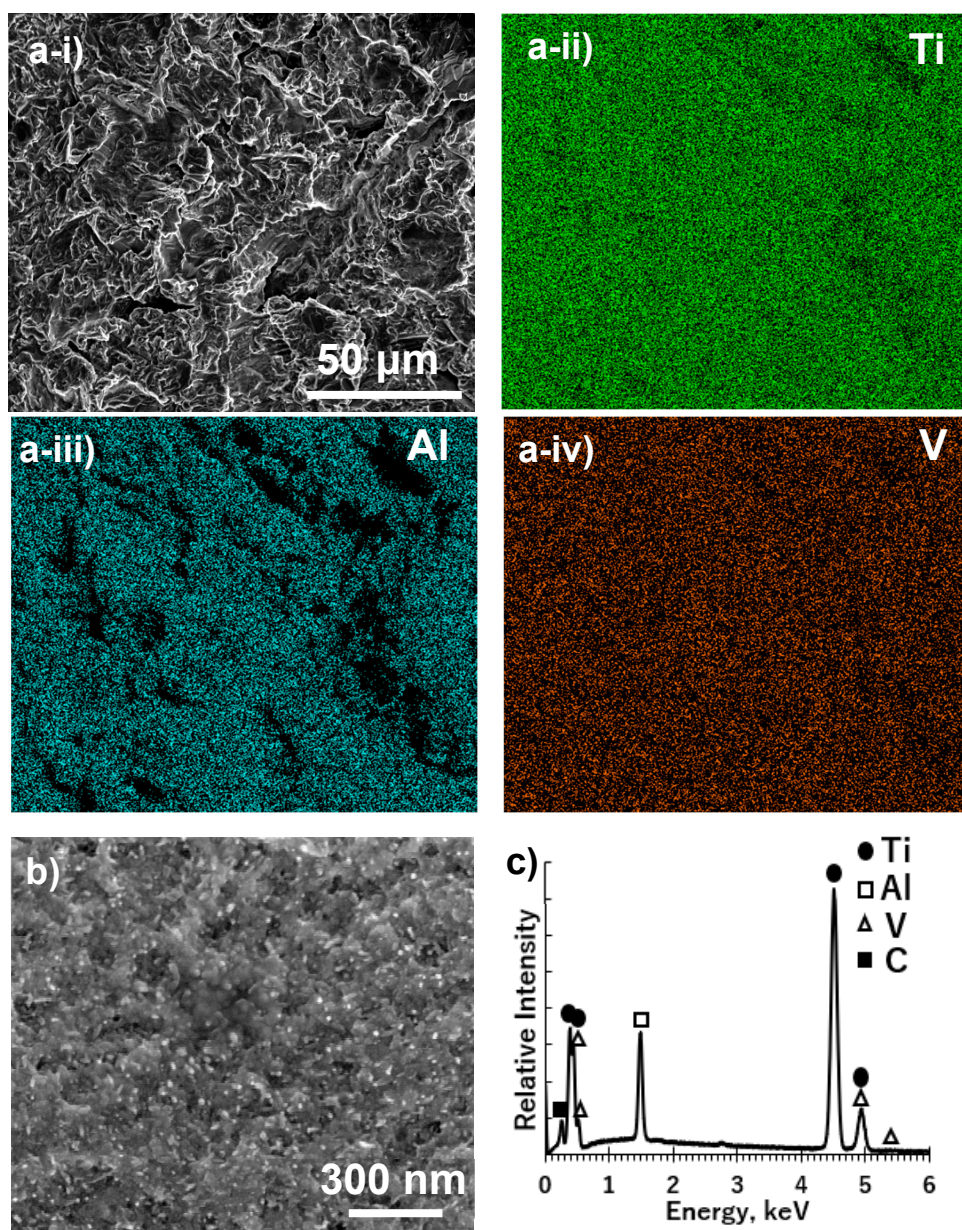


**Supplemental Figure S6.** Characterization of a polished, oxidized DMLS TiAl6V4 specimen after calciothermic reaction at 700°C for 1 h: (**a-i**) top-down BSE image of the surface and associated EDX elemental maps for; (**a-ii**) titanium; (**a-iii**) aluminum; (**a-iv**) vanadium; (**a-v**) oxygen; and (**a-vi**) calcium; (**b**) higher-magnification top-down SE image of the oxidized surface.



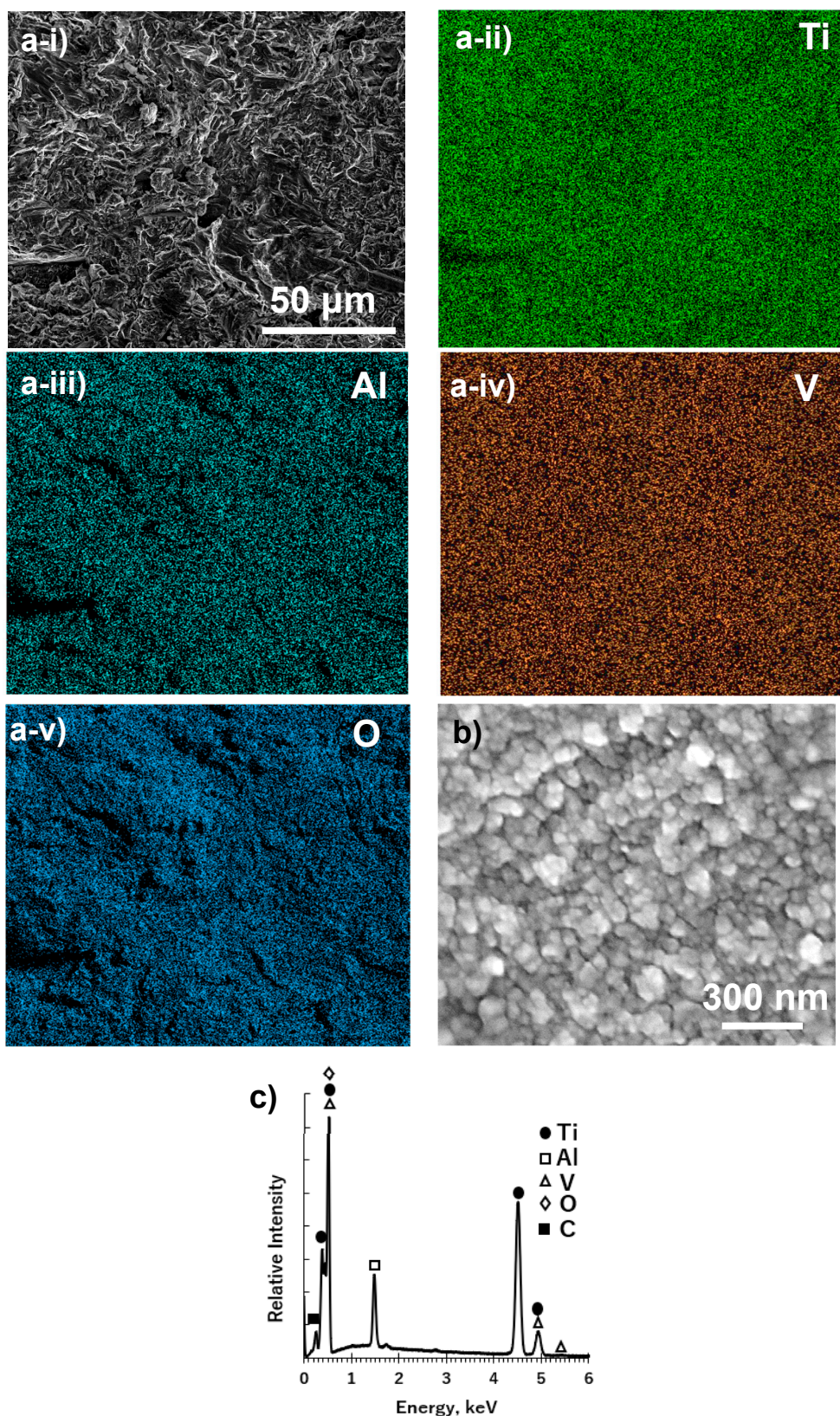
**Supplemental Figure S7.** Characterization of a polished, oxidized, and calciothermally-reacted DMLS TiAl6V4 specimen after selective CaO dissolution: **(a-i)** top-down SEM image of the surface and associated EDX elemental maps for **(a-ii)** titanium, **(a-iii)** aluminum, and **(a-iv)** vanadium; **(b)** Higher-magnification top-down SEM image of the surface.





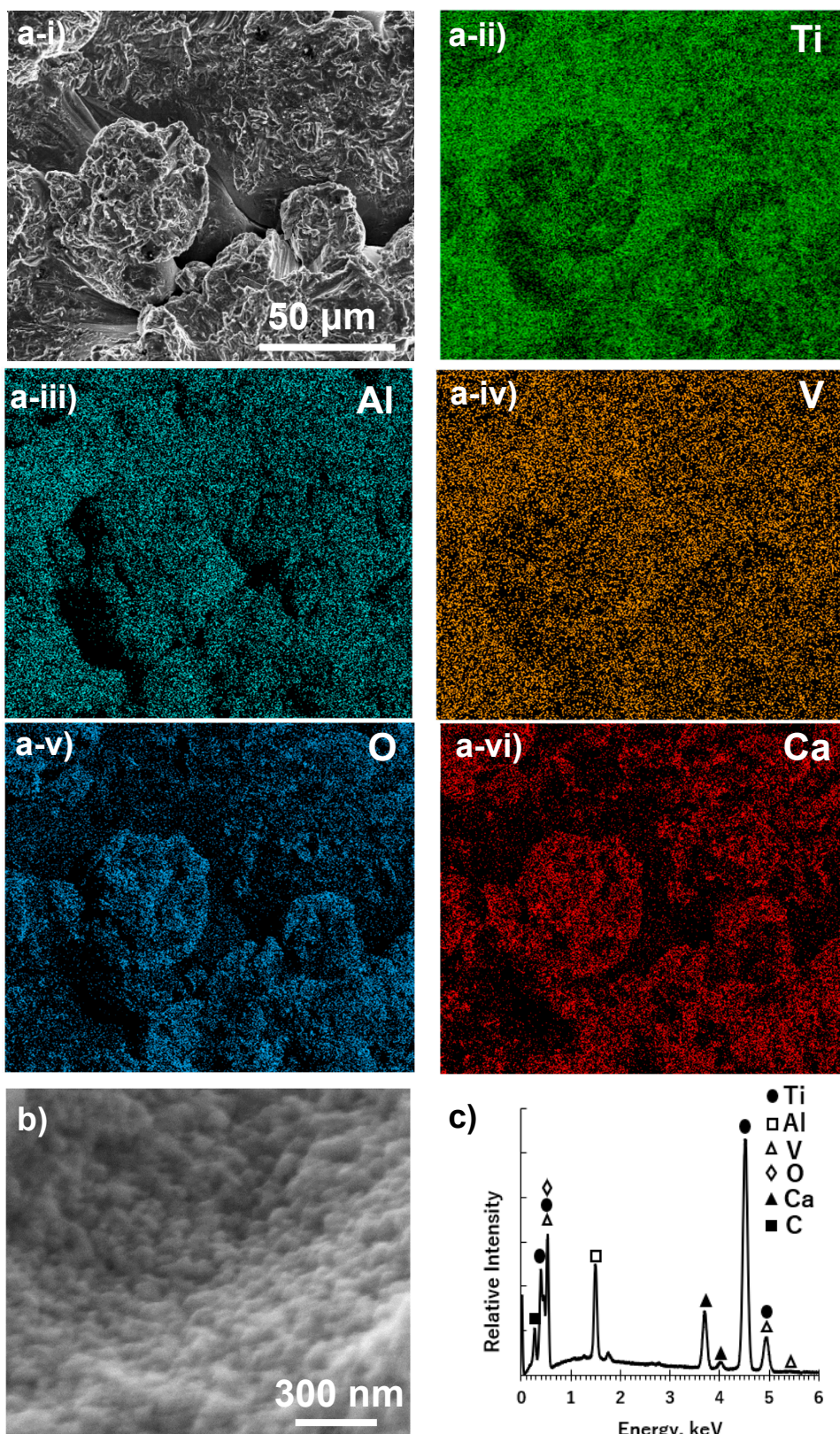
**Supplemental Figure S8.** Characterization of a starting microrough (grit-blasted and acid-etched) DMLS TiAl6V4 specimen: **(a-i)** SEM image of the external surface and associated EDX elemental maps for **(a-ii)** titanium, **(a-iii)** aluminum, and **(a-iv)** vanadium; **(b)** higher-magnification SEM image of the external surface; **(c)** SEM/EDX spectrum obtained from the external surface.





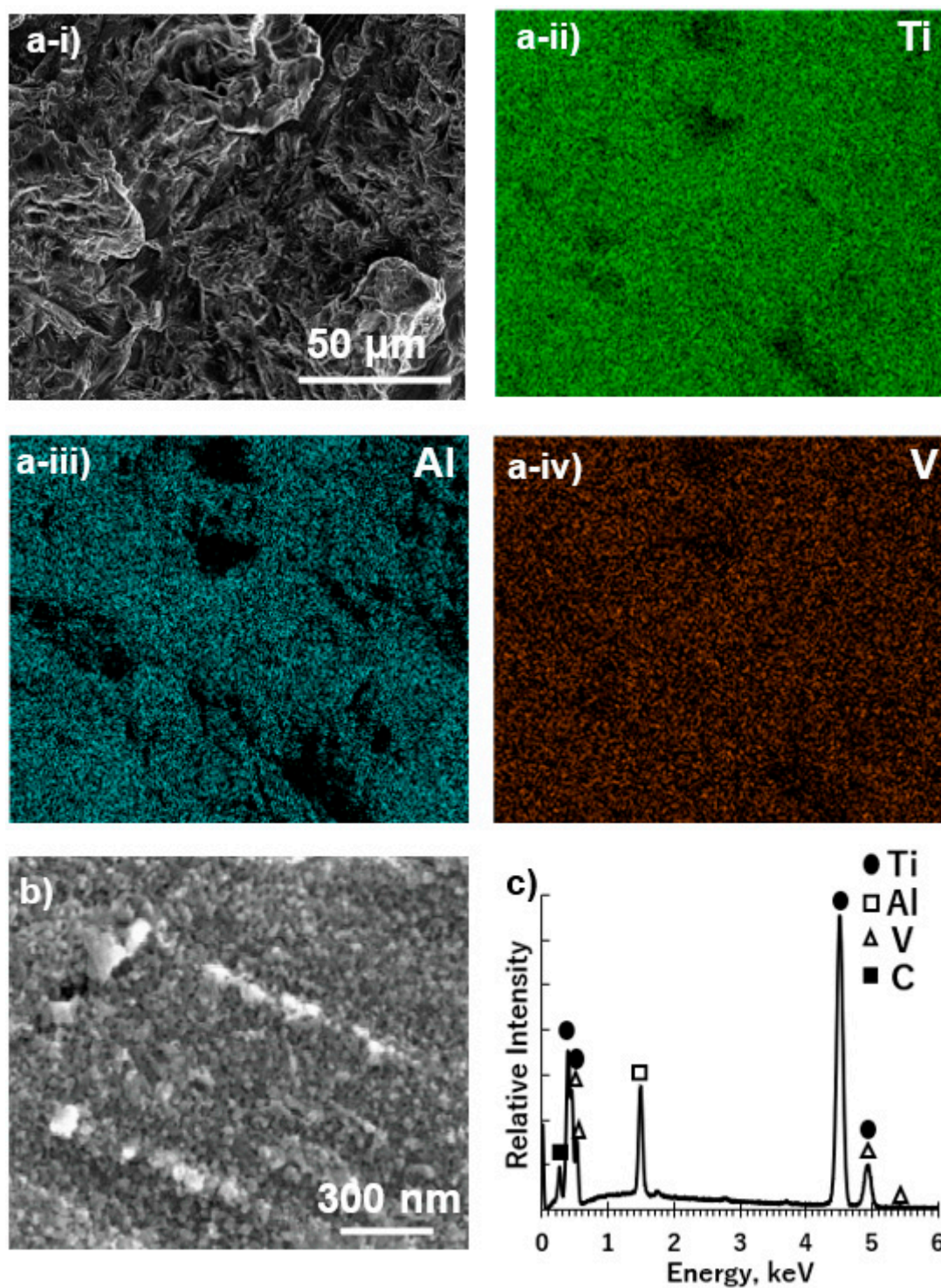
**Supplemental Figure S9.** Characterization of a microrough (grit-blasted and acid-etched) DMLS TiAl6V4 specimen after oxidation in air at 600°C for 6 h: (a-i) SEM image of the external surface and associated EDX elemental maps for (a-ii) titanium, (a-iii) aluminum, (a-iv) vanadium, and (a-v) oxygen; (b) higher-magnification SEM image of the external surface; (c) SEM/EDX spectrum obtained from the external surface.





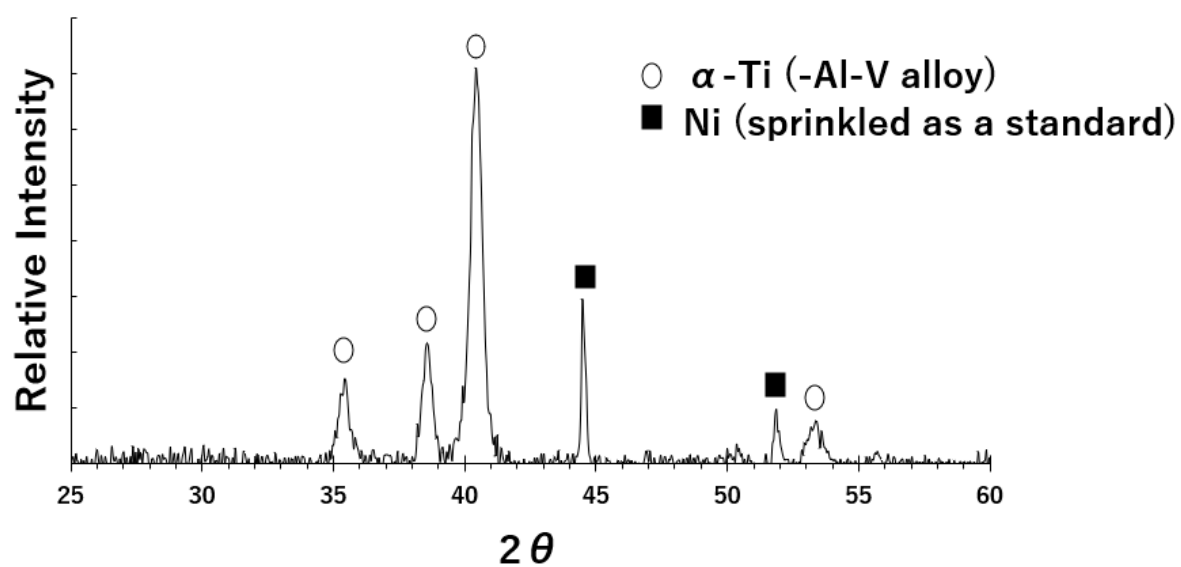
**Supplemental Figure S10.** Characterization of a microrough (grit-blasted and acid-etched), oxidized DMLS TiAl6V4 specimen after calcthermic reaction at 700 °C for 1 h: (a-i) SEM image of the external surface and associated EDX elemental maps for (a-ii) titanium, (a-iii) aluminum, (a-iv) vanadium, (a-v) oxygen, and (a-vi) calcium; (b) higher-magnification SEM image of the external surface; (c) SEM/EDX spectrum obtained from the external surface.





**Supplemental Figure S11.** Characterization of a microrough (grit-blasted and acid-etched), oxidized, calcthermally-reacted DMLS TiAl6V4 specimen after selective CaO dissolution: (a-i) SEM image of the external surface and associated EDX elemental maps for (a-ii) titanium, (a-iii) aluminum, and (a-iv) vanadium; (b) higher-magnification SEM image of the external surface; (c) SEM/EDX spectrum obtained from the external surface.





**Supplemental Figure S12.** XRD analyses of a starting microrough (grit-blasted, acid-etched) DMLS TiAl6V4 specimen.

**Supplemental Table S1.** Normalized compositions obtained from top-down SEM/EDX analyses of the surfaces of TiAl6V4 specimens at various stages of surface modification.

<b>Specimen Condition</b>	<b>Ti (at%)</b>	<b>Al (at%)</b>	<b>V (at%)</b>	<b>O (at%)</b>	<b>Ca (at%)</b>	<b>Ti (wt%)</b>	<b>Al (wt%)</b>	<b>V (wt%)</b>	<b>O (wt%)</b>	<b>Ca (wt%)</b>
As polished (Fig. 2b)	86	10	4	---	---	90	6	4	---	---
After oxidation (Fig. 3c)	38	5	2	55	---	63	4	3	30	---
After calciothermic reduction (Fig. 4c)	43	5	2	43	7	64	4	3	21	8
After CaO dissolution (Fig. 5c)	86	10	4	---	---	90.	6	4	---	---