Supplementary material

Complete morphological series

Surface (upper image in each panel) and cross-sectional (lower image) SEM images of the coatings deposited at pulse duty cycles of 1, 5, 10, 15 and 20%. The three conditions reproduced in Fig. 2 of the main text are marked (a), (c) and (e).

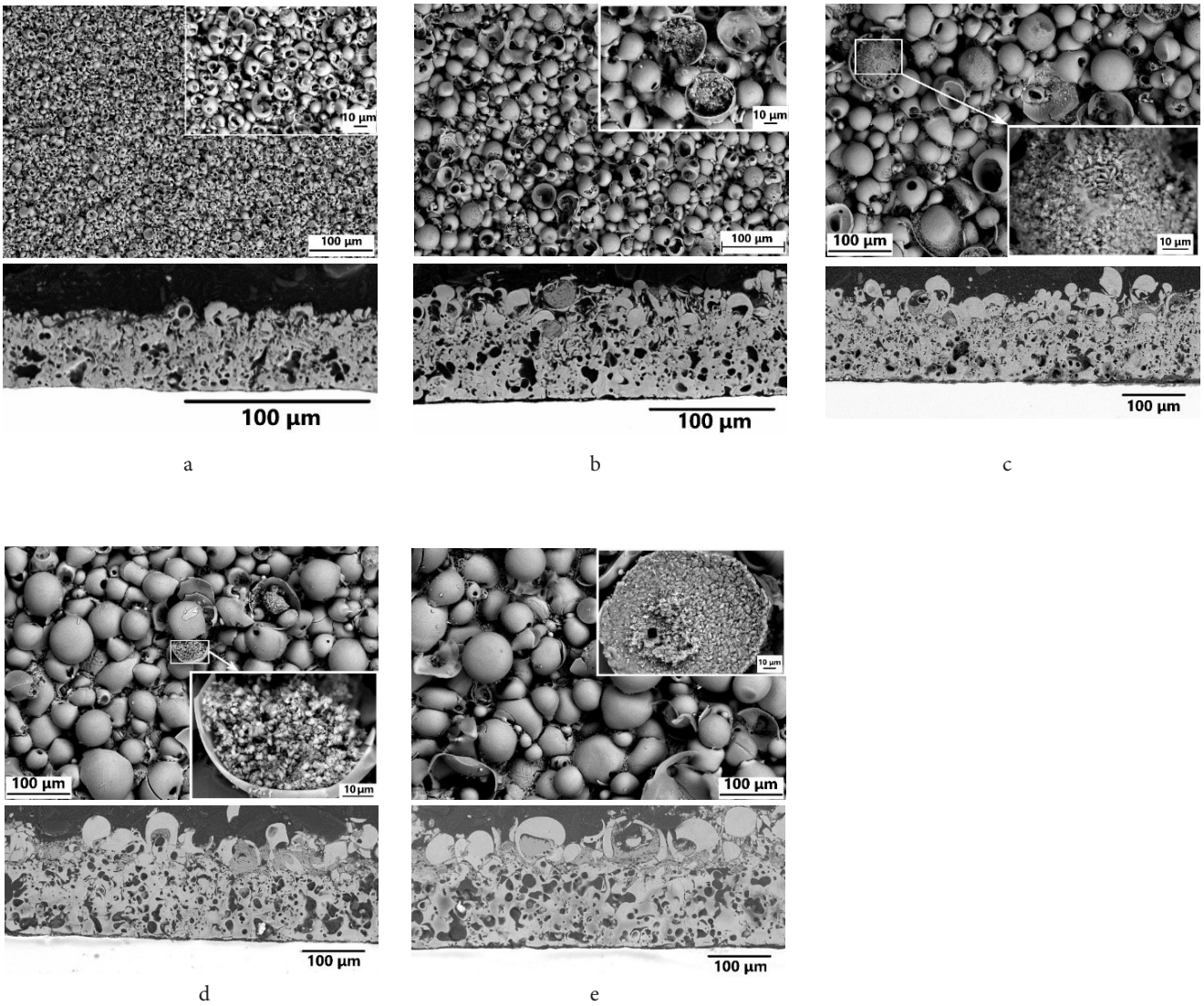
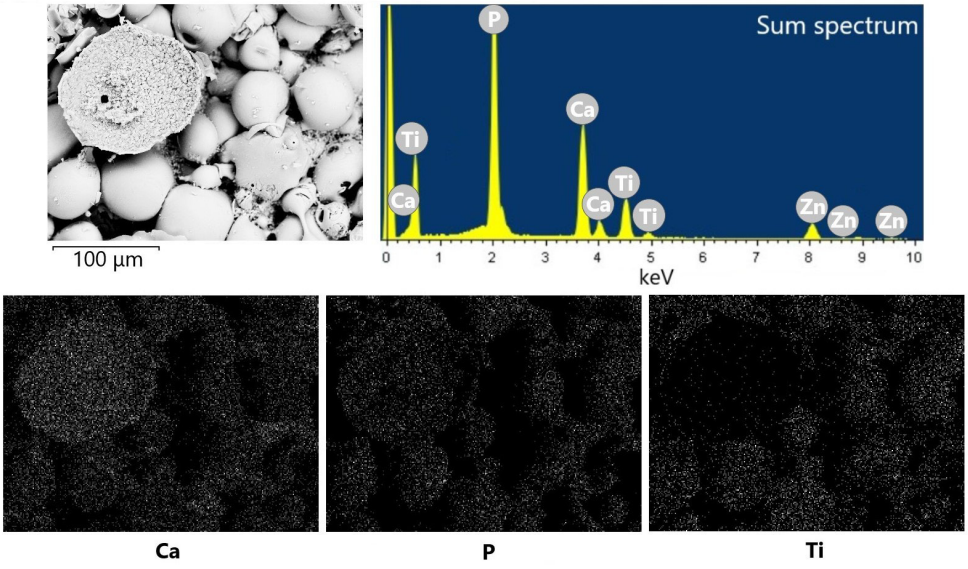


Fig. S1. Surface (upper image) and cross-sectional (lower image) SEM images of the coatings after MAO at duty cycles of 1% (a), 5% (b), 10% (c), 15% (d) and 20% (e).

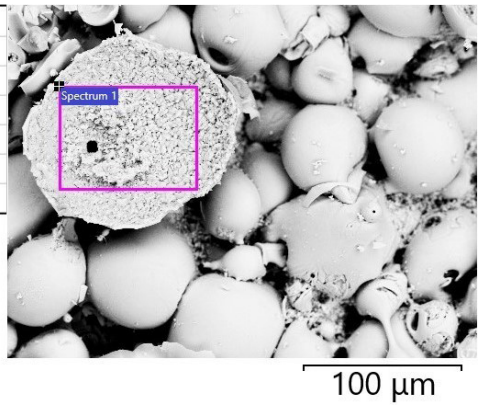
Detailed surface EDX analysis

Element maps of Ca, P and Ti recorded on the coating surface together with the summed spectrum (a), and the selected-area compositions of a fractured spheroid (b) and of an adjacent intact spheroid (c). The fractured feature contains 12.39 at.% Ca and 13.64 at.% P (Ca/P = 0.91), the intact feature 3.94 at.% Ca and 12.27 at.% P (Ca/P = 0.32).

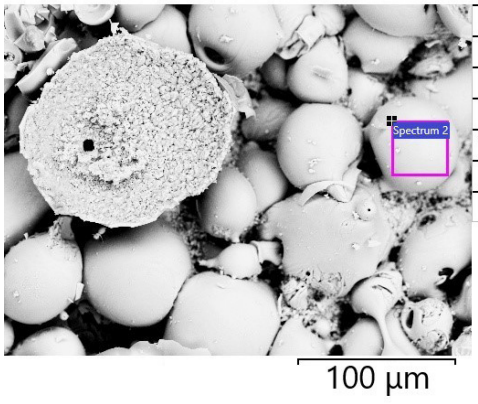


a

Element	at. %
O	73.73
P	13.64
Ca	12.39
Ti	0.08
Zn	0.01
Nb	0.15



b



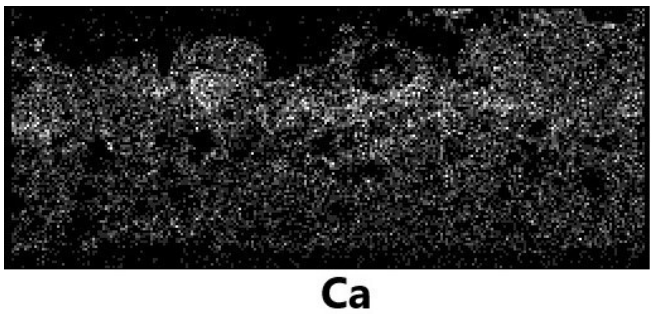
c

Element	at. %
O	77.55
P	12.27
Ca	3.94
Ti	4.38
Zn	0.21
Nb	1.65

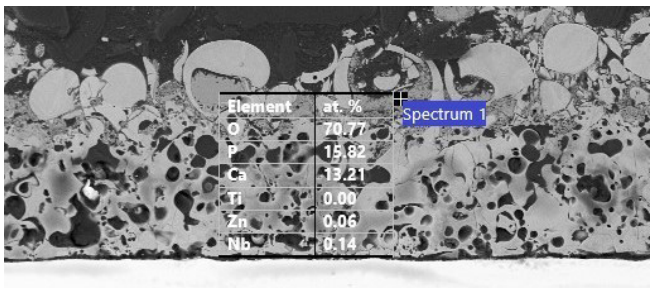
Fig. S2. Surface EDX analysis of the coating deposited at 20% duty cycle: SEM image, sum spectrum and elemental distribution maps of Ca, P, and Ti (a); selectedarea elemental composition of a fractured spheroid (b) and of an adjacent intact spheroid (c).

Detailed cross-sectional EDX analysis

Distribution of calcium across the coating thickness and the local composition inside a fractured near-surface spheroid. The layer-by-layer compositions of the same cross-section are given in Fig. 3 of the main text.



a



b

Fig. S3. Cross-sectional EDX analysis of the coating deposited at 20% duty cycle: distribution map of Ca across the coating thickness (a) and point spectrum analysis inside a fractured near-surface spheroid (b).