Supplementary information for manuscript

Designing and characterization of β-tricalcium phosphate based self-passivating coatings on magnesium alloys

Erdem Şahin [a], Roberta Ruggiero [b], Marco Tatullo [c], Francesco Paduano [b], Meltem Alp [a], Ahmed Şeref [a]

[a] *Department of Metallurgical and Materials Engineering, Muğla Sıtkı Koçman University, TR-4800 Muğla, Turkey.*

[b] *Stem Cells and Medical Genetics Units, Tecnologica Research Institute and Marrelli Health, 88900 Crotone, Italy.*

[c] *Department of Translational Biomedicine and Neuroscience, School of Medicine, University of Bari "Aldo Moro", 70124 Bari, Italy*

Additional Experimental Section

AZ31 plates were immersed in aqueous saturated TCP solutions for 21-day period. The following table gives the results of electrochemical (polarization) tests done after the immersion, on surfaces with deposited phases from the solution. These results represent the maximum corrosion inhibition potential of the depositions that can form from on the immersed samples and were used to design effective cementitious coatings on AZ31 in the later stages.

Table S1. Electrochemical parameters for AZ31 samples with depositions after 21-day immersion in various saturated TCP solutions.

| Sample	Ecorr (mV)	Icorr (µA)	Anodic slope, ba (mV/decade)	Cathodic slope, bc (mV/decade)	Polarization resistance, Rp (Ohms.cm2)	Corrosion rate, (mm/year)
No deposition	-1585.333	201.600	157.233	144.333	162.297	4.443
Saturated TCP soln.	-1583.401	16.208	105.800	246.000	1984.576	0.357
Citrate + saturated TCP soln.	-1316.000	0.132	73.600	116.000	148318.629	0.003
NaCl + saturated TCP soln.	-1352.000	2.805	222.800	163.600	14621.794	0.062
MgNO3 + saturated TCP soln.	-1431.500	1.951	721.100	118.500	22680.693	0.043
HEC + NaCl + saturated TCP soln.	-1383.400	6.695	100.000	183.300	4201.820	0.148
MgNO3 + citrate + saturated TCP soln.	-1236.100	1.037	191.300	182.600	39170.010	0.023

Coated samples immersed in salt solution were subjected to corrosion testing, XRD and SEM analysis, in respective order. The first samples were directly tested for corrosion without being immersed. The change in potential/current curves over time reflects the changes in the coatings in the solution (Fig. S1). The curves of the first samples are located at the far right and the left respectively for RTC and HTC. The current, which is proportional to the corrosion rate, is at its highest level for these samples, only lower than uncoated AZ31 tested under the same conditions. For the RTC set it was observed that the current decreased with immersion time and the absolute value of the voltage increased. The change in voltage indicates a change in surface chemical potential, while the change in current indicates a change in electron transfer rate on the surface, that is mostly related to the coating area of the passive layer. The curves of the 21-day samples showed a regression towards the first curve.
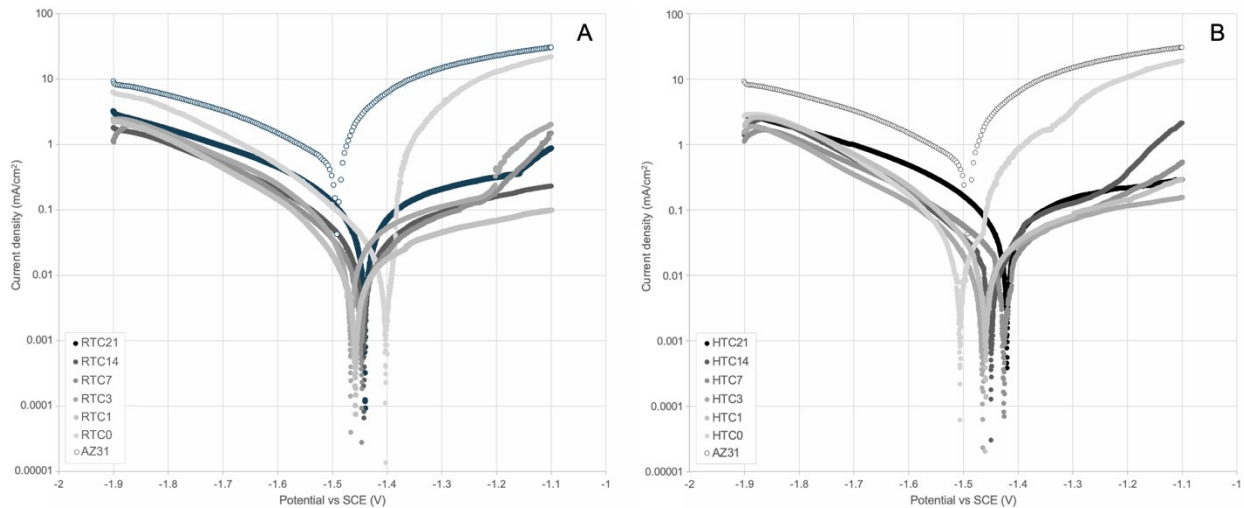
Fig. S1. Polarization curves of RT coated samples (a) and HT coated samples (b) immersed in 3.5wt% NaCl solution.

Coatings dried at 55°C (HTC), have shown slightly better performance than those dried at room temperature (RTC). This may be attributed to cross-linking resulting in an increase in the mechanical and chemical stability of the coating. The potential/current curves seen in Fig. S1B clearly show the beneficial effect of immersion time on passivation as the initial sample gave a curve similar to the uncoated alloy with high negative corrosion potential and high current. Extended immersion reduced both parameters constantly until day 7 and caused subsequent deterioration of the surface.

The quantitative XRD analysis results of the samples given in Fig. S2 reveal the evolving surface composition. The sample surface, initially composed of TCP and magnesium phases, lost some of the coating in the first few days of immersion. With the exposed magnesium surface, magnesium hydroxide and oxychloride phases began to increase. Starting from the third day, it is observed that the magnesium oxychloride phase started to disappear and the surface was increasingly covered with a passive Mg hydroxide phase. The surface of the samples that remained in the salt solution for two weeks has formed a high amount of Mg hydroxide, and other phases only in small amounts presumably at local exposed areas. Fluctuations in the magnesium ratio are due to different amounts of defects and the resulting exposure of the alloy surface.
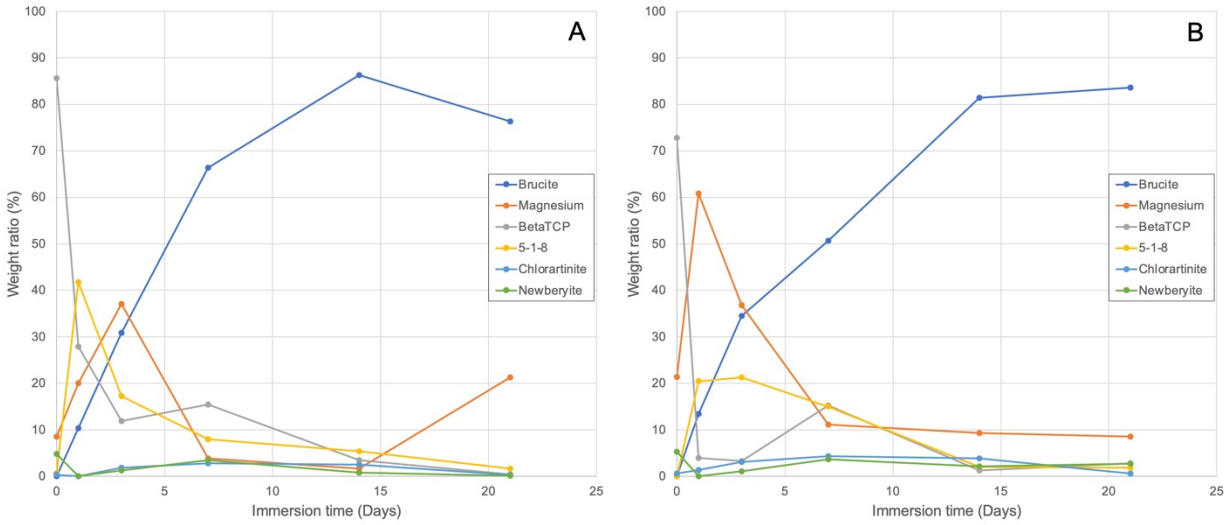
Fig. S2. Phase evolution of the a) RT coated and b) HT coated AZ31 surfaces immersed in 3.5wt% NaCl solution.

Thickness of the dried coatings were measured under an optical microscope. Fig. S3 and Fig. S4 depict the cross-sectional images of the RT coated and HT coated AZ31 samples. The grinding marks are visible on the alloy substrate which was ground together with the coating without mounting in a polymeric sample holder. The wavy surface pattern originates from cutting the coated samples with a steel cutter knife before dip-coating. The averages of ten or more measurements from these samples were found as 118.3 and 187 □m, respectively (Table S2-S3).
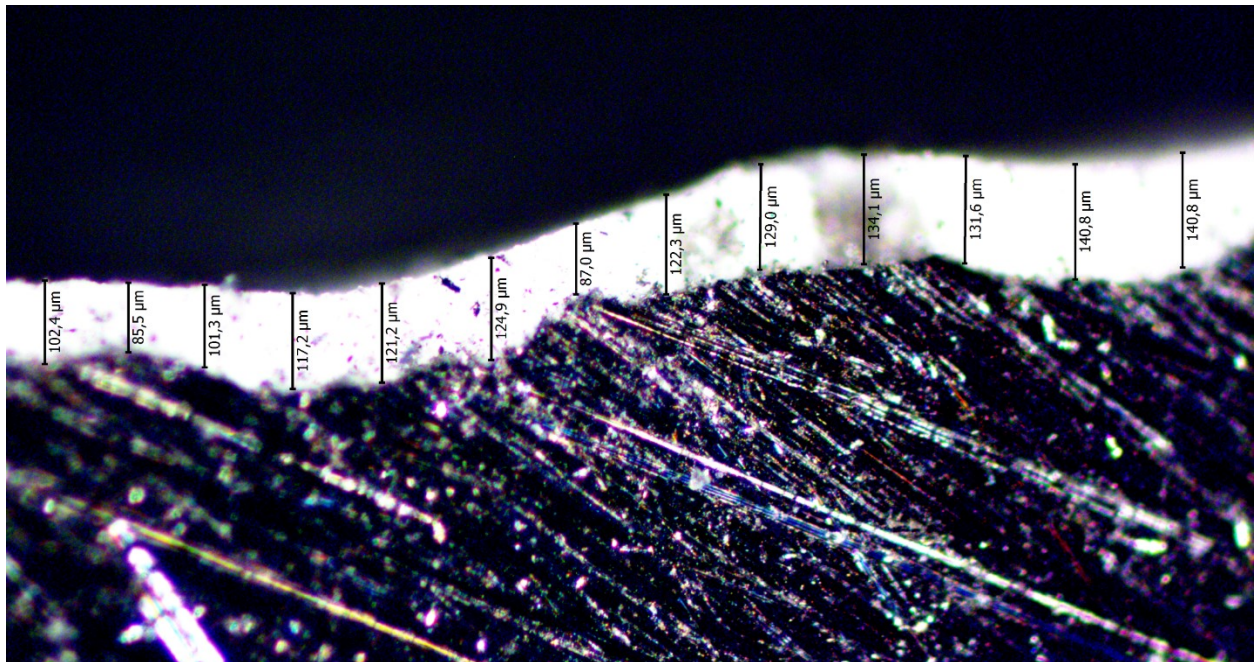
Fig. S3. Cross-sectional optical microscopy image of the RT coated AZ31 sample at 10X magnification.

Table S2. Results of cross-sectional optical microscopy images of the RT coated AZ31 sample.
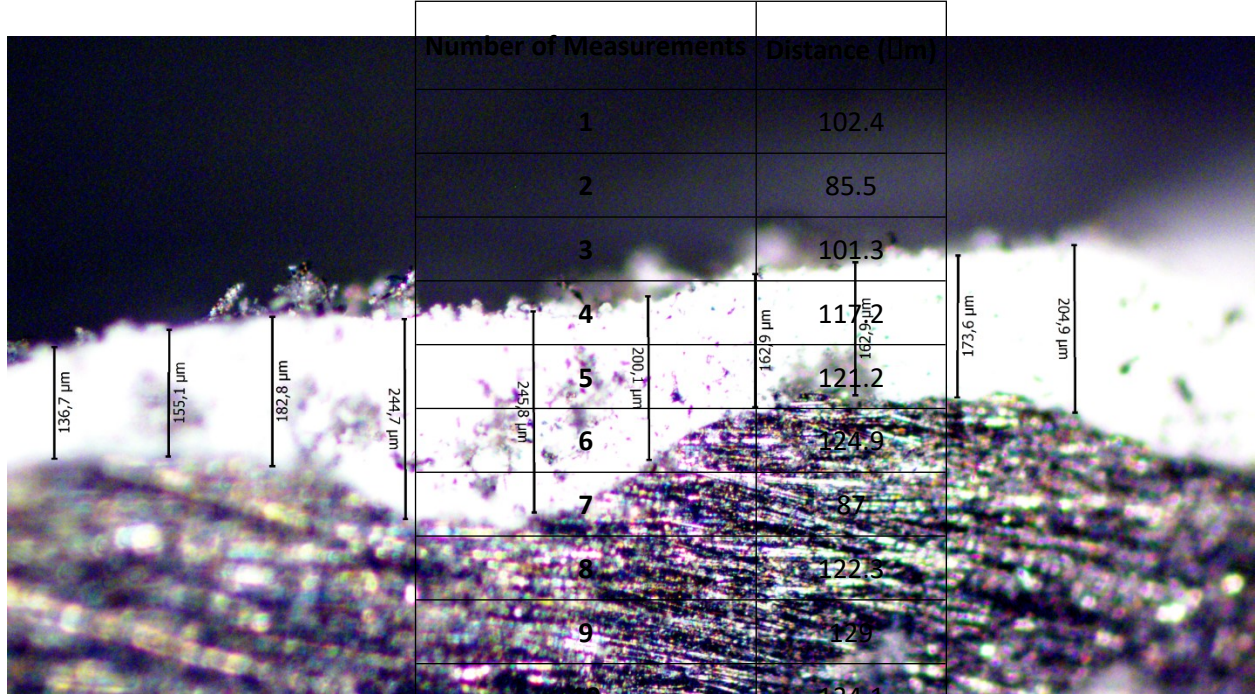
Fig. S4. Cross-sectional optical microscopy image of the HT coated AZ31 sample at 10X magnification.

Table S3. Results of cross-sectional optical microscopy images of the HT coated AZ31 sample.

Number of Measurements	Distance (µm)
1	102.4
2	85.5
3	101.3
4	117.2
5	121.2
6	124.9
7	87
8	122.3
9	129
10	134.1
11	131.6
12	140.8
13	140.8
Average	118.3
Standard Deviation	18.8

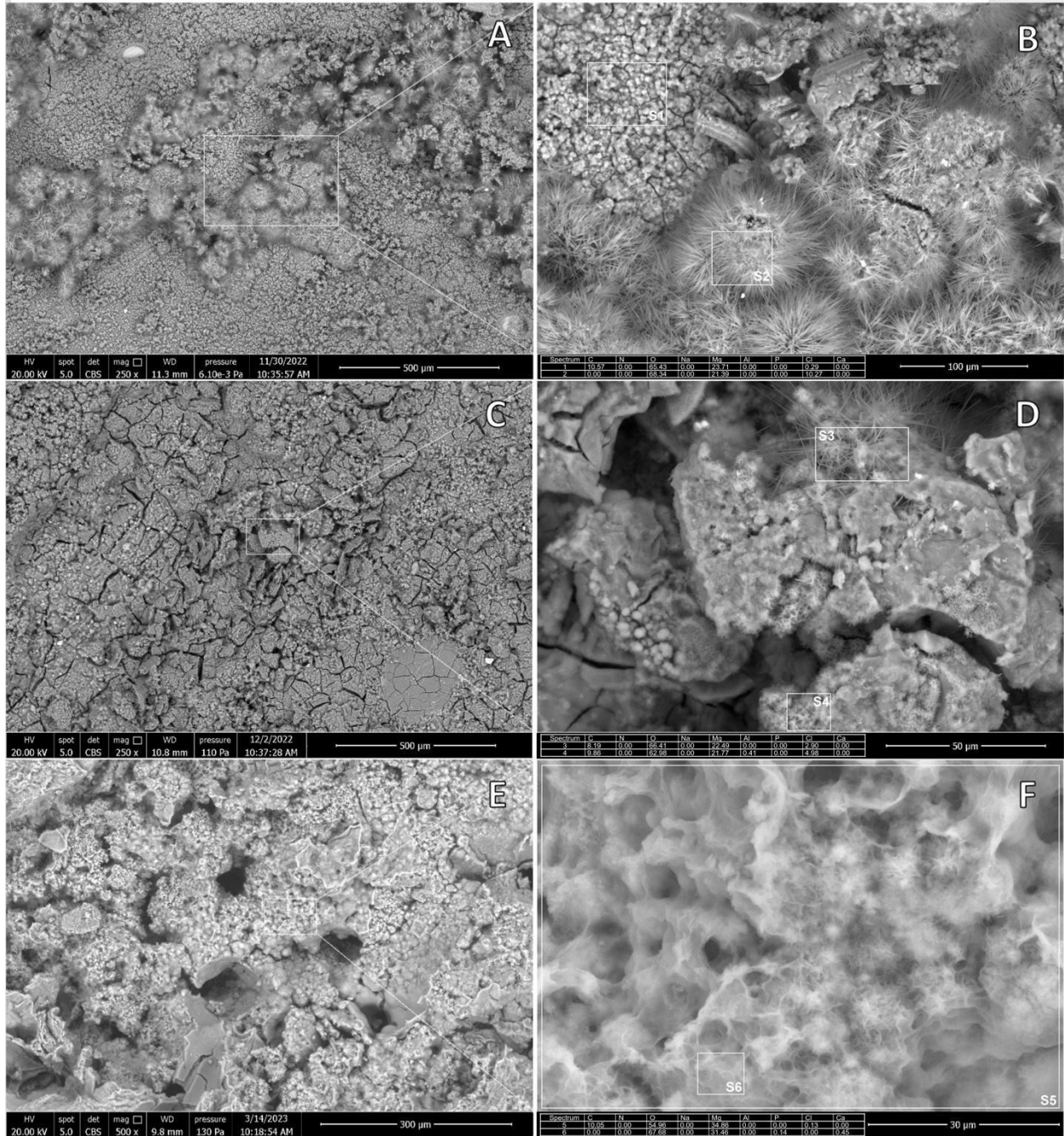| Number of Measurements	Distance (µm)
1	136.7
2	155.1
3	182.8
4	244.7
5	245.8
6	200.1
7	162.9
8	162.9
9	173.6
10	204.9

Average	187
Standard Deviation	36.8

Fig. S5. Side view of double overlap adhered samples prior to testing

The phase transformation of cross-linked and untreated hydrogel coatings in salt solution is shown in Figs. S6 and S7. The surface of the sample immersed for three days shows significant degradation due to chloride attack at the exposed areas. After 7 days of immersion more cracks have appeared on the initially intact surface where Mg oxychloride formations and erosion of the surface were detected (Fig. S6D). In close-up images of Figs. S6 and S7, it is seen that the needle-like magnesium oxychloride crystals growing below lift the layers of the surface separated by cracks. Here pits are created through erosion of the top passive layer after formation of needle-like crystals around the cracks. Metal atoms in the penetrated area convert to oxychloride phase without forming a passivating hydroxide phase, and the crystals growing

vertically break the surface by pushing it up. These structures are found in the EDX analyses to have a 3-1-8 stoichiometry (Mg/Cl=2). It is shown in cement literature that the 5-1-8 (Mg/Cl=3) phase transforms into 3-1-8 over time due to its relative stability. The surface of the sample immersed for 21 days is deeply pitted and heterogeneous. However needle-like magnesium oxychloride crystals were rarely observed. Apparently it started converting from the first day on and has been replaced by Mg hydroxide phases. The surface Mg fraction maximized upon immersion for 21 days, indicating stoichiometric brucite at some points and more than the stoichiometric Mg/O ratio in average (Fig. S6F). This is likely due to the erosion of brucite layer that results in more X-rays detected from the bulk metal.

Panel A — HV 20.00 kV, spot 5.0, det CBS, mag 250 x, WD 11.3 mm, pressure 6.10e-3 Pa, 11/30/2022 10:35:57 AM, scale 500 µm.

Panel B — scale 100 µm.

Spectrum	C	N	O	Na	Mg	Al	P	Cl	Ca
1	10.57	0.00	65.43	0.00	23.71	0.00	0.00	0.29	0.00
2	0.00	0.00	68.34	0.00	21.39	0.00	0.00	10.27	0.00

Panel C — HV 20.00 kV, spot 5.0, det CBS, mag 250 x, WD 10.8 mm, pressure 110 Pa, 12/2/2022 10:37:28 AM, scale 500 µm.

Panel D — scale 50 µm.

Spectrum	C	N	O	Na	Mg	Al	P	Cl	Ca
3	8.19	0.00	66.41	0.00	22.49	0.00	0.00	2.90	0.00
4	9.86	0.00	62.98	0.00	21.77	0.41	0.00	4.98	0.00

Panel E — HV 20.00 kV, spot 5.0, det CBS, mag 500 x, WD 9.8 mm, pressure 130 Pa, 3/14/2023 10:18:54 AM, scale 300 µm.

Panel F — scale 30 µm.

Spectrum	C	N	O	Na	Mg	Al	P	Cl	Ca
5	10.05	0.00	54.96	0.00	34.86	0.00	0.00	0.13	0.00
6	0.00	0.00	87.68	0.00	31.46	0.00	0.14	0.00	0.45

Fig. S6. Surface morphology of HT coated AZ31 after immersion in 3.5wt% NaCl solution for various periods: A, B) 3 days, C, D) 7 days, E, F) 21 days days.
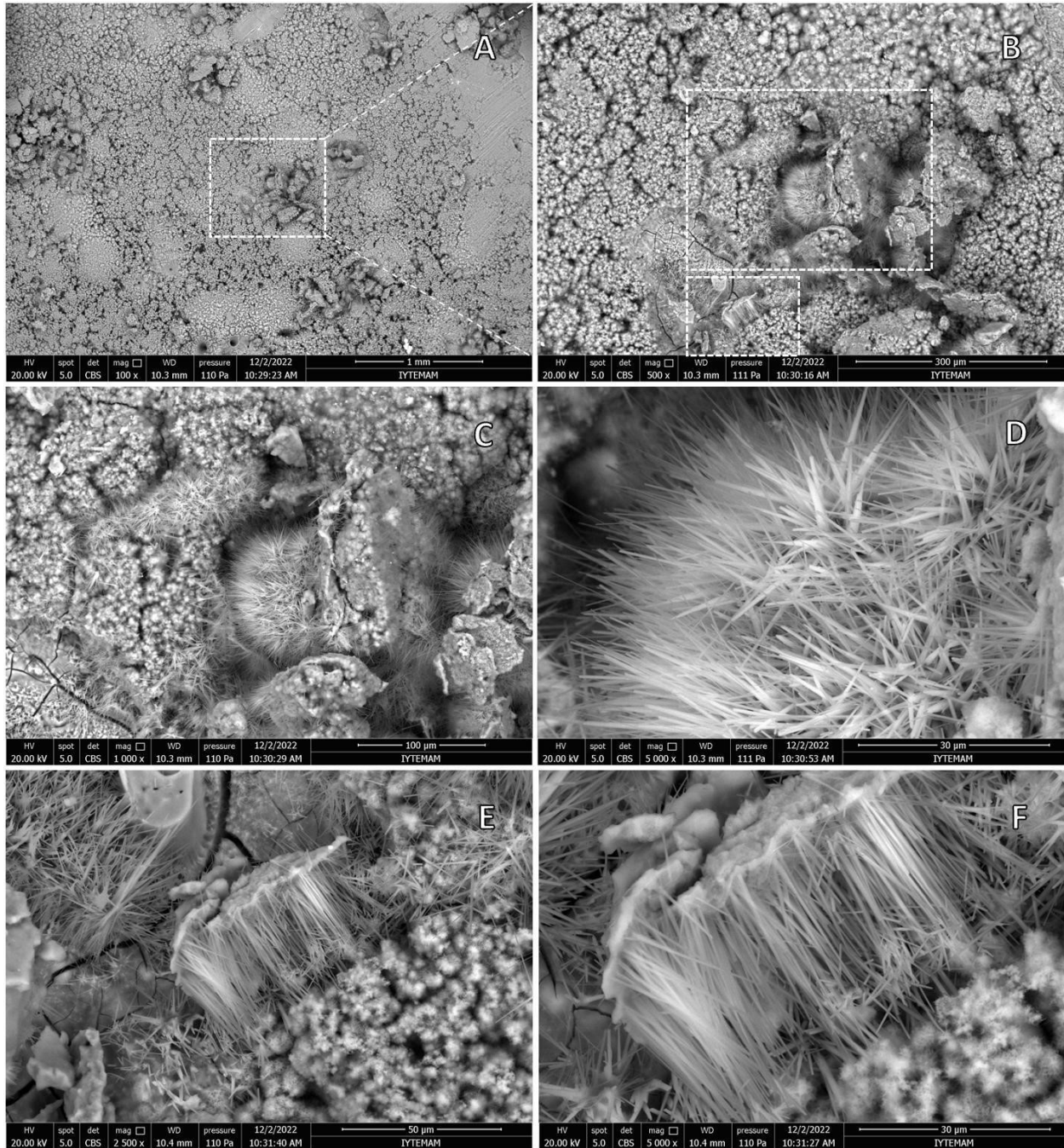
Fig. S7. Surface morphology of RT coated samples 7 days after immersion in 3.5wt% NaCl solution: a) macro view, b) focused image of the degraded zone in the middle, c,d) micro views of the degraded zone in the middle of b, e,f) micro views of the degraded zone at the bottom of b.