Correlative *in situ* synchrotron radiation-based nano CT and (S)TEM imaging of biodegradable Mg-based alloys

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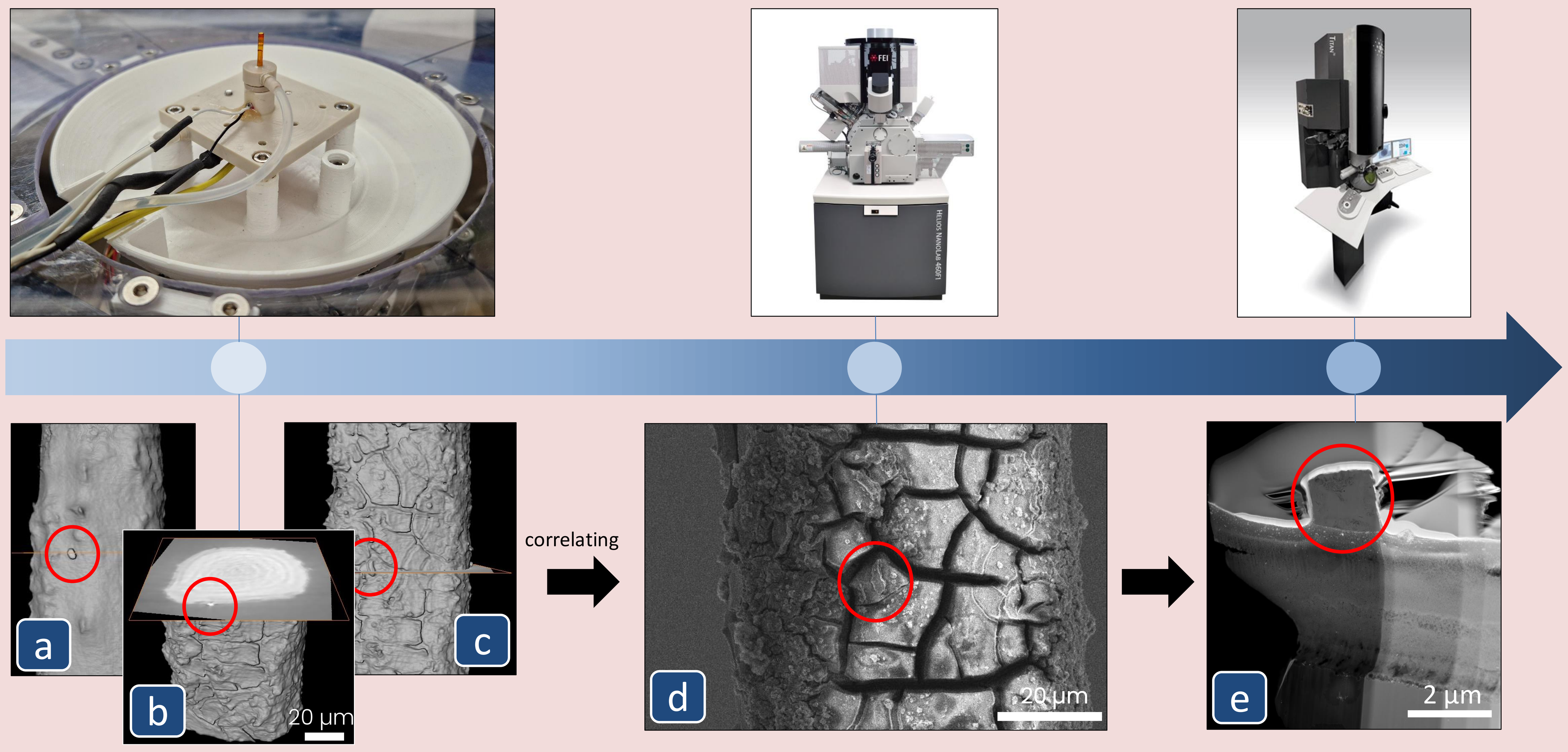
Motivation

Motivation:
Magnesium-based alloys are promising candidates for temporary implants due to their biocompatibility and natural biodegradability, which eliminates the need for surgical removal after healing. However, a significant challenge remains: the rapid and uneven degradation of Mg alloys in physiological conditions often compromises their structural stability, which makes it difficult to achieve controlled, uniform degradation throughout an implant lifespan. A comprehensive understanding of how alloy microstructure impacts degradation behavior is essential to advancing these alloys for safe and effective biomedical use.

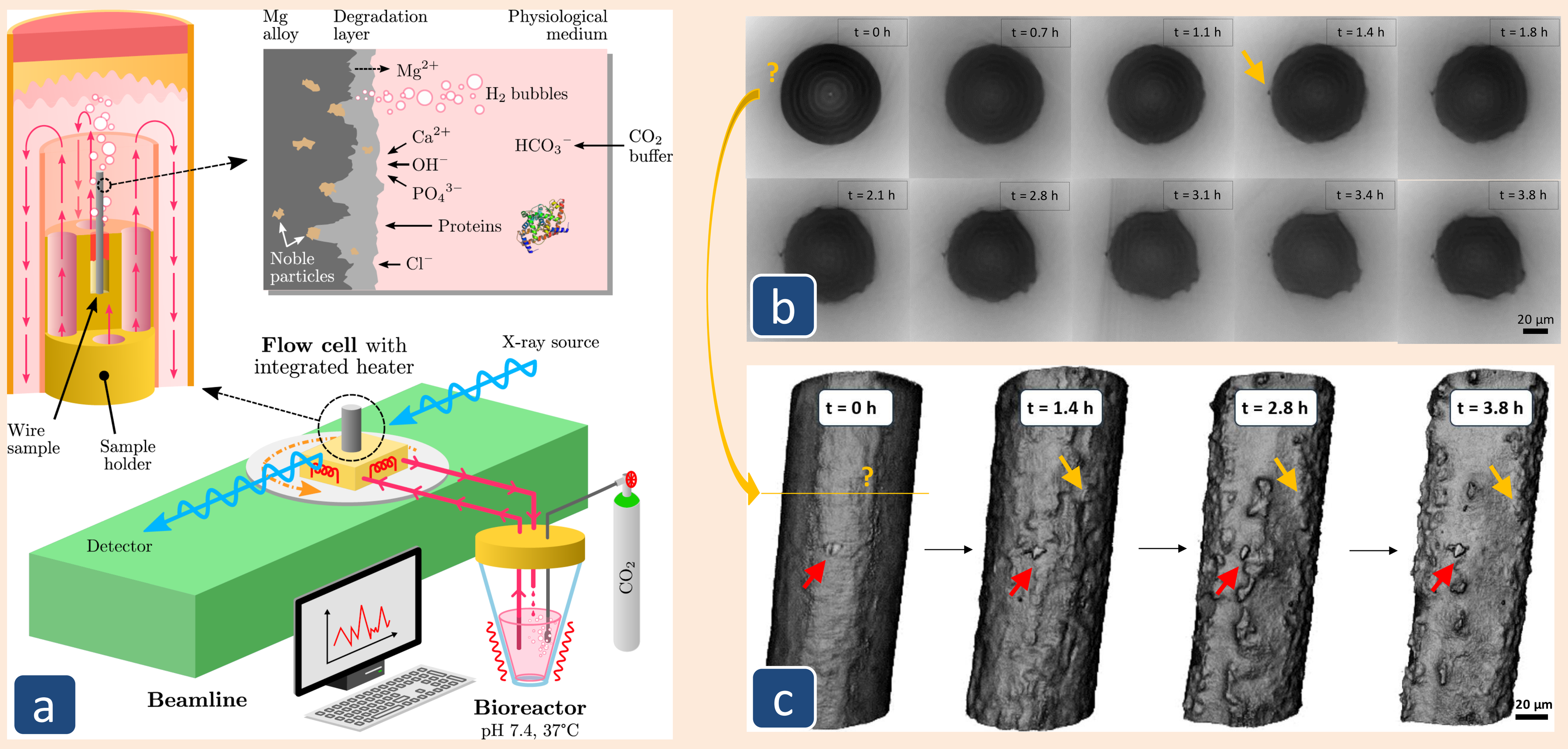
Gap and Aim:
This study addresses the critical need for a multiscale approach to Mg alloy degradation, focusing on the roles of alloy microstructure and local chemical environments. By combining *in situ* SRnanoCT with correlative (S)TEM, this research aims to visualize the degradation process across both macroscopic and atomic scales. SRnanoCT provides 3D insights into the spatial and temporal progression of degradation, while STEM identifies impurities, phase boundaries, and compositional variations. This correlative methodology offers a comprehensive framework for understanding how microstructural features affect degradation, ultimately guiding the design of Mg-based implants with controlled, predictable degradation profiles.

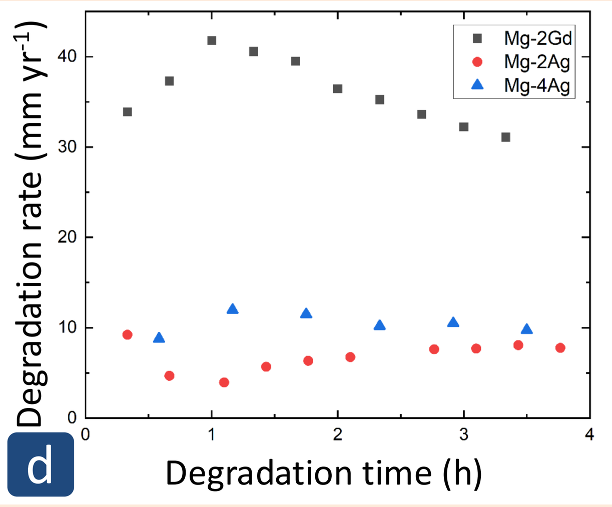
Correlative workflow



The basic principle of a correlative workflow for in situ SRnanoCT with (S)TEM investigations of a Mg wire from left to right. At the top are flow-cell setup at the synchrotron [1], dual-beam FIB-SEM and (S)TEM. At the bottom are volume renderings of (a) wet sample, (b, c) matched dried sample, (d) correlated SEM image and (e) HAADF image of TEM lamella. The red circles indicate the correlated ROI (particle).

In situ biodegradation SRnanoCT imaging





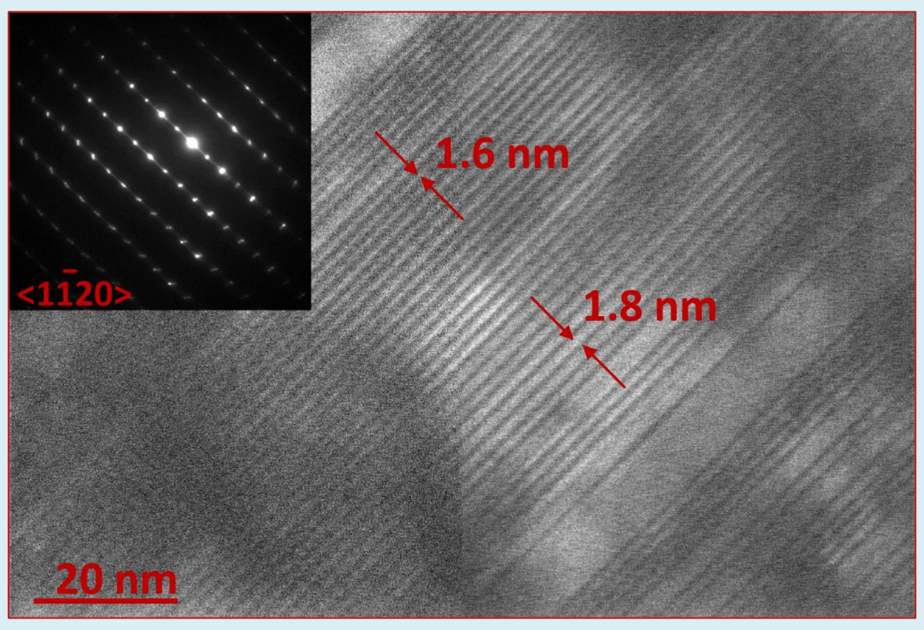
Mg-based alloy degradation in simulated body fluid over time: (a) Schematic overview of the degradation process using the in situ flow-cell setup.[1] (b) In situ SRnanoCT slices of a Mg-2wt.%Ag wire at different time points of degradation from (c) corresponding volumetric renderings. Orange arrows indicate a precipitation formation and red arrows an impurity particle. (d) Degradation rates of varying alloying composition compared.

[1] Taken from J. Reimers and H. C. Trinh et al., ACS Appl. Mater. Inter.,15 (29), 35600-35610 (2023)

Quantitative analysis of degradation rates reveals clear distinctions between alloy compositions, with Mg-2wt.%Gd degrading faster than Mg-2,4wt.%Ag, and higher silver content correlating with an increase in degradation rate. SRnanoCT imaging highlights the heterogeneous degradation behavior along the wire sample, particularly in regions with larger particles, such as impurities and precipitates, which exhibit a significant macroscopic influence on the corrosion process. However, SRnanoCT has limitations in fully characterizing these particles, as their precise composition and impact on the degradation mechanism remain unclear. To address this, complementary electron microscopy techniques are necessary to provide detailed compositional information and confirm the nature of these particles, offering deeper insights into their role in the alloy's degradation dynamics.

POF V - Outlook

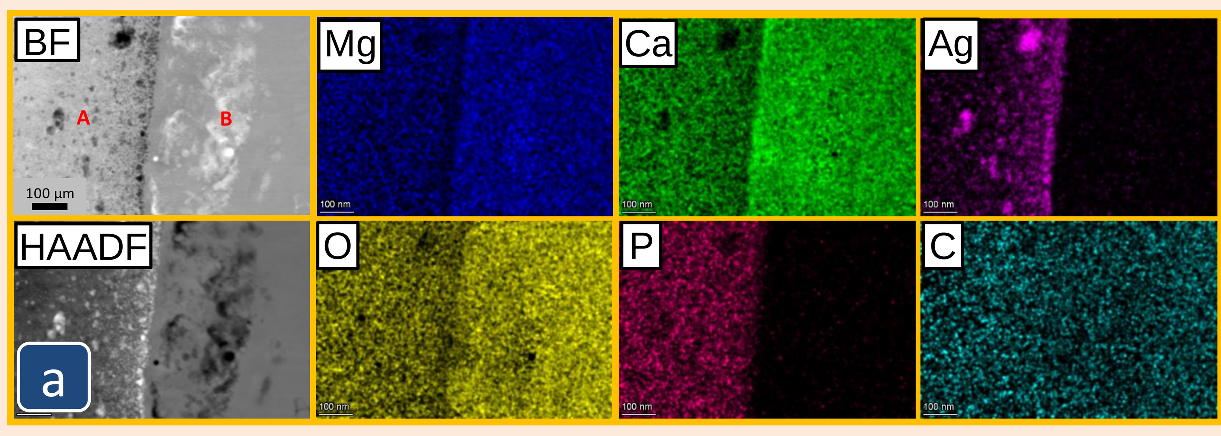
The mechanical properties of Mg can be substantially improved by the addition of Y and Zn. Favourable processing conditions lead to the formation of a Long Periodic Stacking Ordered Structure (LPSO) that provides superior strength without deteriorating the ductility. Complemented with the biocompatibility of Mg-Y-Zn (WZ) alloys makes them suitable as biodegradable implant materials. Further alloying elements modify the secondary phases, enabling to tune the property profile. In order to investigate the effect of minor alloying additions on the microstructure of the LPSO phase and the macroscopic behaviour of the material under service conditions, a multiscale correlative approach as developed here is necessary where in situ µCT is combined with nano-tomography and TEM investigations.



LPSO phase in Mg1.8Y0.6Zn in as-extruded state. The TEM investigation shows the co-existence of the 18R (1.6 nm) originating from casting and 14H (1.8 nm) as a result of partial phase transformation during the processing.

Due to the newly developed multiscale correlative approach of combining SRnanoCT and TEM techniques new insight could be generated. In POF V, this will be expanded to other sample systems to study the hierarchical influence of parameters in structures like Mg alloys containing LPSO phases or biological materials like bone.

Correlative (S)TEM investigations

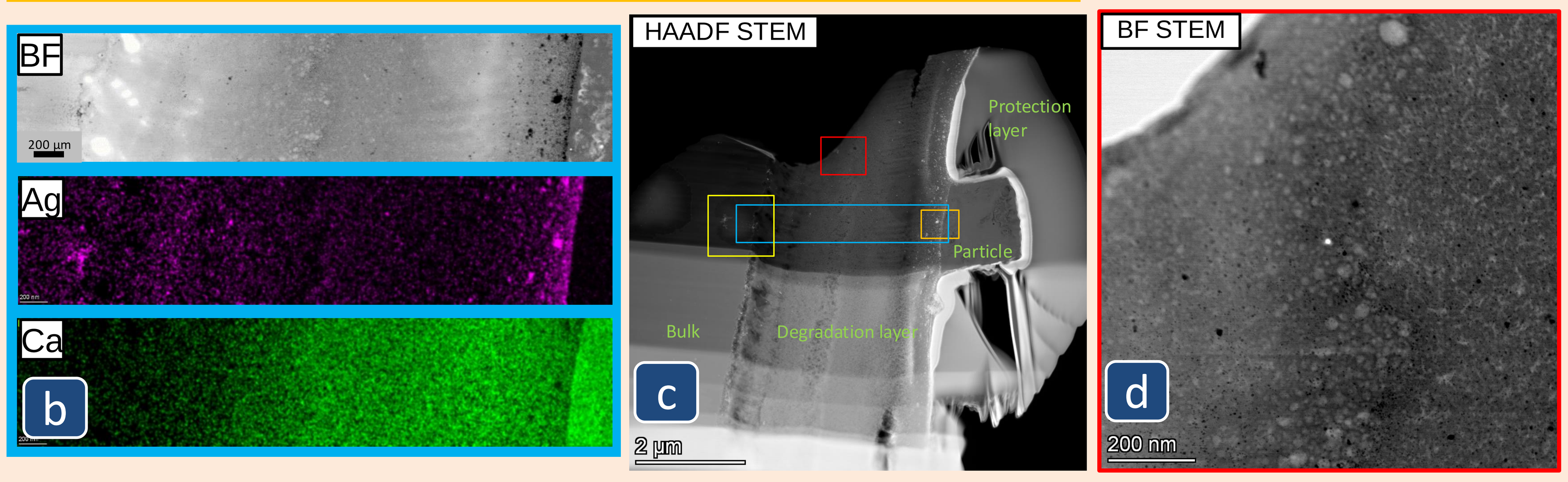


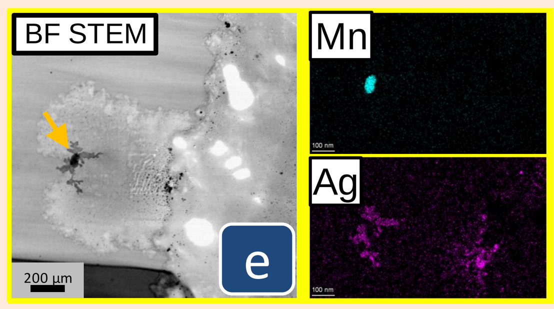
Degradation layer (A)

Element	Mass fraction (%)
C	8.31
O	29.34
Mg	7.35
P	10.11
Ca	31.23
Ag	13.66

Particle (B)

Element	Mass fraction (%)
C	5.20
O	39.15
Mg	11.21
Ca	44.37





STEM investigations revealing various information about the degradation structure of a Mg-2wt%.Ag TEM lamella: (a) BF and HAADF image of degradation layer – particle interface with corresponding two-dimensional distribution of the chemical elements (EDX maps of Mg, Ca, Ag, O, P and C). To the right are elemental distributions of (A) degradation layer and (B) particle. (b) BF image along the lamella – (left) bulk, (middle) degradation layer and (right) particle with EDX maps of Ag and Ca. (c) Overview of the lamella with marked areas. (d) Porosity change within the degradation layer. (e) Mn-rich impurity (arrow) inside the bulk material with EDX maps of Mn and Ag.

HAADF and BF imaging highlight Ag-rich regions throughout the degradation layer (DL), with more concentrated and larger Ag areas observed near the DL-precipitate interface. Along the DL, porosity analysis reveals larger pores near the bulk-DL interface, possibly due to hydrogen gas formation during degradation. As one moves outward from the interface, pores transition into a denser, possibly layered network, which could reflect either distinct degradation phases or an artifact from sample drying, where the DL may collapse, altering observed porosity patterns. Notably, the Mn-rich impurity within the bulk material appears to significantly impact local corrosion, with visible deeper degradation around this area compared to Mn-free regions. The Mn-rich impurity may act as a localized galvanic cell, promoting redistribution of Ag around the site and resulting in distinctive Ag patterning, indicative of localized electrochemical interactions.

Conclusion

The *in situ* SRnanoCT scans highlighted heterogeneities in the degradation layer and varying degradation rates influenced by alloy composition. The ROI-based (S)TEM analysis provided insights into precipitate stability, degradation layer morphology and microstructural defects, helping to form an understanding of the degradation pathways.

Non-destructive 3D imaging offers dynamic information on:
- Degradation rate
- Formation of the degradation layer
- Degradation homogeneity
- Activity of larger particles and pores

Correlative high-resolution imaging provides insights into:
- Elemental and structural distribution within the degradation layer
- Porosity differences across different degradation regions
- Revealing sub-surface features that contribute to heterogeneous degradation patterns
- Mapping of corrosion pathways

Challenges for correlative imaging:
- Sample transfer
- Identification of regions-of-interest for focussed ion beam milling
- (Automated) image registration between NFHT, (S)TEM and EDX

Acknowledgement

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