

Chemical and Structural Degradation of SS 316 Thermal-Cycled in Chloride/Carbonate Bath

Yanting Yin¹, Raihan Rumman¹, David Lewis¹, Gunther G. Andersson¹

¹*Flinders Institute for Nanoscale Science and Technology, Flinders Microscopy and Microanalysis, Flinders University, Adelaide SA 5042, Australia*

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E-mail: yin0069@flinders.edu.au

Investigating the degradation of stainless steel 316 as a containment material for phase change materials (PCM) is crucial to the comprehensive design of solar thermal energy storage systems. In our work stainless steel 316 alloy tokens were half-immersed in a carbonate/chloride (NaCl/Na₂CO₃) based PCM. The set of samples were then thermally cycled up to 500 times (in total 1500 hours) at a high temperature between 550 °C to 700°C, at which the PCM changed its phase from solid to liquid and vice-versa. Air or nitrogen were used for the environmental gas as a comparison. In addition to the existing characterisations, limited information can be found for a fundamental characterisation of the oxidation state of steel alloys due to thermal cycle. This is due to the lack of technique for either removing the interference of PCM on the surface or creating characterisation inside the bulk of corrosion layer.

In our work, the change of chemical state over a controlled depth was characterised and the cross-section of the corrosion layer was studied with a combination of spectroscopy and microscopy. In situ sputtering with X-ray photoemission spectroscopy was applied to the tokens to investigate the level of corrosiveness, by probing the oxidation states and other chemical bonds of the token surface. With the capability of sputtering, characterisation can also be performed at a range of different depths into the outermost layer of corrosion surface. Different species of FeO_x were found at the corrosion layer-Fe(OH)_x, Fe₂O₃, Fe₃O₄, FeO and Fe. Study showed a gradient distribution of oxidation state of Fe at the corrosion surface. The proportion of heavy oxidised species, such as Fe₂O₃, increased at the outermost layer. Meanwhile, in response to the increase of thermal cycling time, higher oxidised state of Fe was also observed, indicating a severer degradation of token surface. By investigating the cycled PCM, passivation materials of stainless steel-Cr and its variables-Cr₂O₃ were found depleted into the PCM as a consequence of thermal cycling. The depletion increased in proportion to the increase of cycling time. Scanning electron microscopy with energy-dispersive X-ray analysis was further performed on the well-polished cross-section of the tokens. Element distribution and morphology across the section from outermost layer into alloy bulk were characterised with line scans. Due to the thermal cycle, Cr migrated to the alloy surface and oxidised as a passivation layer. The thicknesses of such layers can be extended to a maximum thickness of 90-120 μm after 500 thermal cycles. However, with PCM bath, the Cr kept depleting from the top surface into PCM, leaving Fe unprotected and oxidised to FeO_x variables corrosion. The thickness of corrosion layer increased with increasing cycling time and showed no saturation with 500 cycles.

Such Cr depletion was the main cause of the formation of corrosiveness to stainless steel 316. Upon the suspended token part, the depletion still occurred due to the vaporisation of PCM but less than the immersed section. The thicknesses of corrosion layers were rather similar with air and N₂ cycling, but with N₂ ambient, the Cr₂O₃ layer was noticeably narrowed. A small degree of O₂ and H₂O in N₂ can be still destructive to the alloys because the proportion of oxidant is not enough to form a dense Cr₂O₃ layer with adequate thickness, but incurs oxidation to Fe once the Cr is depleted.

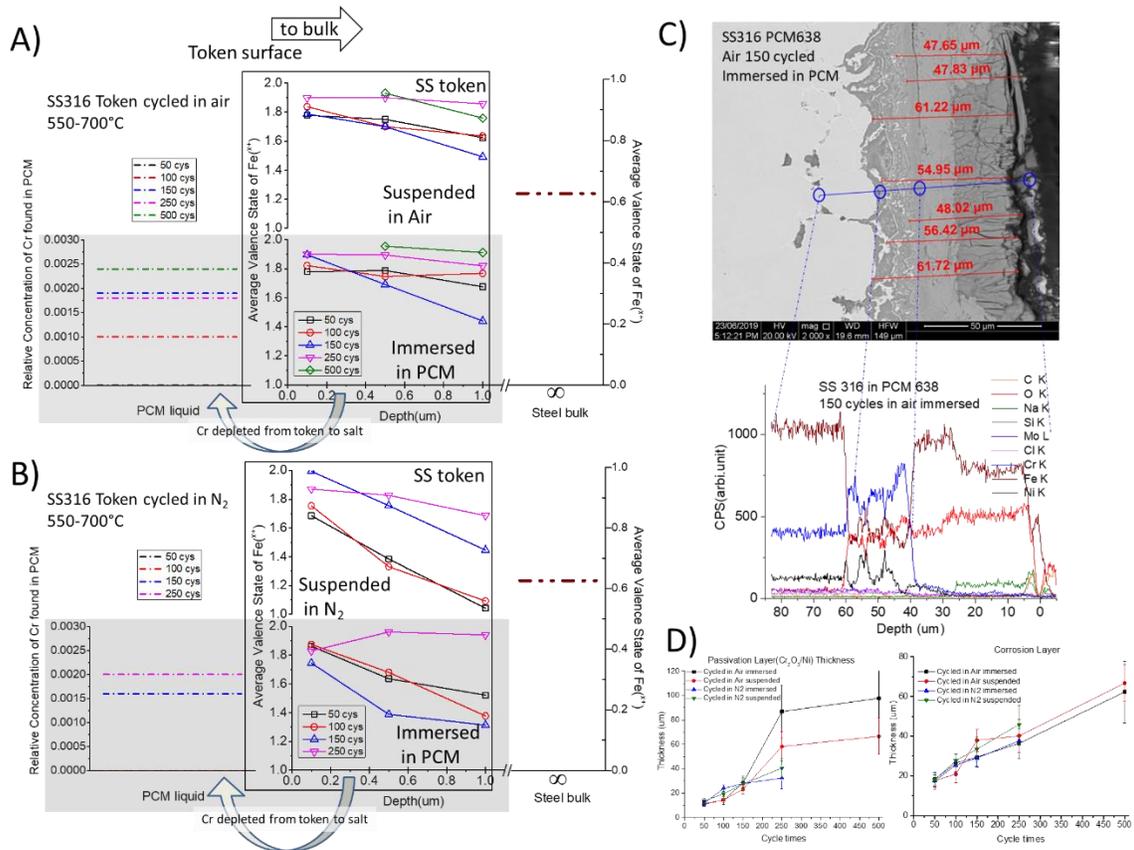


Figure 1. A) B) illustration of oxidation of Fe across the outermost layer; C) line scan with element distribution over the interface; D) plot of Cr₂O₃ layer and corrosion layer thicknesses because of thermal cycling