Phase Change and Formation of Interfaces of SS 316 in PCM Salt Bath

Raihan Rumman\textsuperscript{a}, Yanting Yin\textsuperscript{a}, David Lewis\textsuperscript{a}, Gunther Andersson\textsuperscript{a}

\textsuperscript{a} Flinders Institute for Nanoscale Science and Technology, Flinders Microscopy and Microanalysis, Flinders University, Adelaide SA 5042, Australia, Funded by Australian Solar Thermal Research Institute
Email: Raihan.rumman@flinders.edu.au

Stainless steel 316 (SS 316) is widely used as a material for containing purpose of phase change materials (PCM) in solar thermal storage due to their cost-effective and lasting microstructural features. Two PCM mixtures (710: KCO\textsubscript{3} and Na\textsubscript{2}CO\textsubscript{3} and 638: NaCl and Na\textsubscript{2}CO\textsubscript{3}) have been used to study their reactive behaviour against SS 316, followed by further comparisons. In terms of their high latent heat and stability under high temperature, such chloride/carbonate mixtures can be considered as appropriate PCM salts.

In this work, SS 316 alloy coupons were immersed in the PCMs inside a non-reactive, refractory crucible. Given that the eutectic melting temperatures for the PCMs were 710 °C and 638 °C respectively, the cycling temperatures were kept between 650 °C to 750 °C and 550 °C to 700 °C in atmosphere. The During the cyclic loading, both PCM salts repeatedly changed their phases from solid to liquid and retuned to solid phase. The coupons experienced a range of cycling times, from 50 to 500 cycles, in response to increasing exposure time in salt bath.

X-ray diffraction was applied on the coupons with different cycles to identify the peak distributions, and phase and space structure of the corrosion products that were found on most samples. The results in Fig 1 (A) showed that the presence of heavily oxidised Fe\textsubscript{2}O\textsubscript{3} in hematite alpha phase increased with increasing thermal cycles, while the intensity of Cr\textsubscript{2}O\textsubscript{3} -R3/c phase decreased. Other peaks including FeO, Fe\textsubscript{3}O\textsubscript{4} and their space structure were also observed during the analysis. Based on the presence and intensity of the peaks, it is evident that Fe-based oxidation increased with time, indicating severe degradation on the material.

Scanning electron microscopy with energy-dispersive X-ray analysis and Auger electron spectroscopy were carried out on finely polished cross-sections of the coupons. Elemental distribution and line scanning along cross-section were also analysed, as illustrated in Fig 1 (B). Due to the use of high temperature cycles, Ni and Cr from the alloy seemed to have migrated towards the surface, where Cr oxidised to Cr\textsubscript{2}O\textsubscript{3} at the surface because of its high chemical potential in presence of O\textsubscript{2}. Presence of such Cr\textsubscript{2}O\textsubscript{3} layer is thought of as a passivation front against further migration of Ni and Fe in the bulk, and reactions with oxidants, such as O\textsubscript{2} and H\textsubscript{2}O. However, with continuous cycling in PCM, Cr on the coupon surface depleted and eventually dissolved into the liquid PCM. As a result, oxidant from atmosphere penetrated into the surface and oxidised the steel alloys, forming a corroded layer. A distribution highly-oxidised Fe can be observed, which peaked at the outermost layer and decreased, going towards the metal.

In Fig 1 (C), a deep penetration of oxidant into the bulk has been probed with elemental mapping upon the interfaces, as a result of thermal cycling in atmosphere. Such oxidant is likely to oxidise Cr through formation of Cr\textsubscript{2}O\textsubscript{3} (Fig 1 (D)), preventing further Fe oxidation traveling inwards. However, the nature and quantity of Cr\textsubscript{2}O\textsubscript{3} can also deteriorate the mechanical strength of the alloy. Hence, the formation of Cr\textsubscript{2}O\textsubscript{3} has a double-sided influence on the overall life-time of stainless steel used for high temperature containment material.
Figure 1. A) Identification of X-ray diffraction result of cycled SS 316; B) Formation of corrosion layers along cross section due to thermal cycling; C) Elemental mapping of cross-section; D) Line scan of cross-section showing elemental distributions.