Study of Microstructure and Chemistry of Interface Formation on SS 316 as CSP Containment for Alkaline Salt with

Microscopy and Spectroscopy Methods

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Outeline

Research Aim

The work focused on the degradation upon microstructure and chemical properties of stainless steel 316 thermal cycled at high temperature in alkaline salt mixture.

1) Experimental and methodology setup
2) Sample preparation
3) Microstructure analysis and interface formation
4) Comparison of microstructure of SS316 cycled in different gas and salt mixtures
5) Depth-resolved chemical analysis and phase formation
6) Conclusions
Methodology

Scanning electron microscopy (SEM) with back-scattered electron Z-contrast
Energy dispersive X-ray spectroscopy (EDAX)
X-ray photoelectron spectroscopy (XPS) with sputtering process
X-ray diffractometer (XRD)
Sample Setup

Containment used: Stainless steel 316

Phase change materials used:

PCM638: NaCl:Na$_2$CO$_3$ (45:55) cycled 550-700 °C

PCM710: Na$_2$CO$_3$:KCO$_3$ (50:50) cycled 650-750 °C

Flow gas control: air and N$_2$ flow unsealed oven

SS316 in token shape immersed in PCM thermal cycled in given temperature range in an unsealed oven

Cycled for individually 50, 100, 150, 250 and 500 times

Air (atmosphere) and N$_2$ was separately used for filling the oven

After thermal cycles:

SS316 cut into piece and PCM grinded for spectroscopy analysis

SS316 tokens sealed in epoxy and polished for exposing the cross-section of the interfaces for microstructure analysis
Formation of interfaces were clearly seen

Ni/Cr/Fe/O different behaviors
Line Scans of Interface Formation

Thermal cycled in air with PCM 638 as examples
Line scans with SEM+EDAX
Grain etching layer can be observed
Oxidant penetrated into SS316 bulk and chemically reacted along the grain boundary
Ni/Cr$_2$O$_3$ enriched, Cr depleted/Fe oxide layers can be measured
Comparison of Interface Formation (Different PCM, Different Gas Ambient)

Different cycles: interface layer thicknesses increase

Different gas: $\text{Cr}_2\text{O}_3$ layer thickness, oxidant penetration equal

Different PCM: PCM710 builds up thicker $\text{Cr}_2\text{O}_3$ layer, oxidant penetration obstacle
Formation rate in air flow with PCM638:
\( \text{Cr}_2\text{O}_3: 0.15 \text{ um/cycle} \)
\( \text{FeO}_x \text{ with Cr depletion: } 0.13 \text{ um/cycle} \)
Uncorroded token thickness loss: 0.12 um/cycle

Formation rate in N\(_2\) flow with PCM638
\( \text{Cr}_2\text{O}_3: 0.04 \text{ um/cycle} \)
\( \text{FeO}_x \text{ with Cr depletion: } 0.12 \text{ um/cycle} \)
Uncorroded token thickness loss: 0.11 um/cycle

\( \text{N}_2\) flow with a small residue of oxidant will not prevent corrosion upon SS316
Remaining Unsolved Questions:

1) **Actual chemical bond? How do we know from SEM, is that \( \text{CrO}_x \)? \( \text{FeO}_x \)? Or \( \text{NiO}_x \)? formed at the interface. How can we determine the binding form of oxygen**

2) **Surface layer phase change, any structure crystalinity alters due to thermal cycles?**
Chemical Characterisations for Unsolved Questions

Depth-resolved XPS:
- **O**: metal-oxide, carbonate
- **Fe**: Fe, FeO, Fe$_3$O$_4$, Fe$_2$O$_3$, Fe(OH)$_x$
- **Cr**: Cr$_2$O$_3$ (also found in PCM)
- **Ni**: Ni, NiO, Ni$_2$O$_3$

Average oxidation state of Fe illustrated a decreasing trend with a probing depth increases.

Bulk Ni was mostly Ni metal, but oxidised on outermost layer.

Cr$_2$O$_3$ across the whole layer.
Surface Microstructure and Phase Characterisations

X-Ray Diffraction
PCM638 SS316 in Air

Different phase of elemental crystalinity presents
On top of that, Sigma phase of Fe-Cr-O found
which is critically fragile
Conclusions

1) Ni, Cr migrated due to thermal cycle in PCM (increase of entropy), Ni not overlapping with Cr while Cr migrated faster (molecular free path)

2) On surface, Ni, Fe and Cr were strongly oxidised. Cr was mostly depleted into PCM resulting in Fe unprotected and further oxidised

3) In SS316 bulk, oxidant penetrated deep, oxidising mostly Cr along the grain boundary

4) A migration-depletion-oxidation-penetration-etching cycle formed during thermal cycling, which is the major issue of alloy containment for PCM storage of CSP (thickness loss due to Fe oxidation and mechanical fragility due to grain etching)

5) $N_2$ flow into the oven barely protected the corrosion. $Cr_2O_3$ protection layer did not form in sufficient thickness due to lack of $O_2$ but a small content of oxidant will still penetrate and etch the grain

6) Further space-resolved and far-depth resolved methods are currently under preparation
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