Chapter 7: Conclusions

The initial aim of this work was to investigate the possibility that stainless steel could be utilised within a molten salt nuclear fission reactor. Previous work has focused primarily on nickel superalloys which have been used in two previous molten salt reactors, but with the advancement of stainless steel design, it was postulated that this material could be utilised.

Numerous authors have previously investigated molten salt corrosion in both fluorides and chlorides and also numerous different nickel superalloys and stainless steels. It was reported in this body of literature that, due to halides (fluoride and chloride) acting as fluxing agents, any impurities within the salt would result in the protective layer dissolving. It was also stated that after 500 hours the corrosion rate would reduce as the impurities within the salt have been utilised in the corrosion mechanism.

Experimental work in this thesis initially utilised stainless steel 316L and a ternary eutectic salt, LiCl-NaCl-KCl, at 600°C for one day. This was done to ensure the alloy could withstand the molten salt environment. Impurities were present as the experiments were run in atmospheric air. Subsequently, further tests were run with stainless steel 316L over one, three, four and six weeks, with the three week test being repeated due to an anomalous result.

The samples were analysed using surface and cross sectional SEM/EDX analysis along with XRD. Generally, it was found that as immersion time increased, the percentage mass loss also increased, and this is attributed to the selective leaching of chromium. In the majority of the stainless steel 316L tests lithium chromium oxide (LiCrO$_2$) formed over the stainless steel sample and acted as a protective layer. The percentage coverage of the corrosion layer over the sample increased as immersion time increased. In addition to spinels forming on the surface, iron chloride also appeared in the repeated three week tests and the six week tests. As immersion time increased, the presence of iron oxide diffusing into the bulk also became apparent in the cross sectional SEM/EDX data. This implies that although the lithium chromium oxide (LiCrO$_2$) layer does not appear to attack the surface when it first forms, reactions can and do take place with the bulk as immersion time increases.

The initial three week tests were at first considered to be anomalies with the formation of five different corrosion products. The visual tests show a brown/black corrosion product forming a thick scale over the sample. The SEM image shows the formation of a blocky crystal product which consists of a mixture of chromium/iron oxides and chlorides. This result was originally expected as literature stated that a stable corrosion layer could not be formed.

Chapter 4 investigated the role of lithium within stainless steel 316L corrosion with a molten salt. Two different salt mixtures were used, LiCl-NaCl-KCl and NaCl-KCl. The ternary tests all showed the
formation of a stable lithium chromium oxide (LiCrO$_2$) layer. The binary tests showed a higher percentage weight loss and the formation of a thick corrosion layer made up of mixed oxides, Cr$_2$O$_3$, Fe$_2$O$_3$ etc., and blocky crystals. Again, the three week test showed the formation of a new corrosion layer containing sodium, iron and oxygen and was made up of tabular crystals. This was only ever seen in this environment, and when the experiment was repeated the results were analogous to the results obtained at one week. The four week tests also shows the formation of blocky oxides, and appeared to show iron oxide extending into the bulk.

Finally, due to the incorporation of chromium within the corrosion layer, the compositional effects of the steel itself were addressed. Three further materials were tested: 304L, LDX2101 and iron. It was found the smallest percentage mass loss is attributed to the sample with the highest chromium content LDX2101, but this could also be caused by spalling of the corrosion layer. Stainless steel 304L, which has a higher percentage of chromium compared to 316L, formed LiCrO$_2$ with a smaller percentage coverage compared to stainless steel 316L. Therefore, it can be concluded that although chromium does leach out of stainless steels to form protective corrosion layers, the selective leaching and subsequent protection do not solely rely on the chromium content of the sample. Iron was also investigated and despite the lack of alloying additions it fared relatively well.

This work has shown that although it has previously been stated that a stable corrosion layer cannot be formed due to chlorides and fluorides acting as fluxing agents, it is in fact possible to form a stable corrosion layer if lithium is incorporated. Although this does show promise for the future of molten salt reactors, the presence of lithium within a reactor can cause issues as tritium can form if lithium-7 is not solely used. This work has also indicated that although selective leaching of chromium is usually responsible for the formation of a corrosion layer, the presence of other constituent elements also plays an important role in the formation of the corrosion layer. It is therefore proposed that it may be possible to refine the elemental compositions of stainless steel to give a thick protective corrosion layer with a high percentage coverage and minimal spalling. Finally, anomalous results have been seen continuously throughout this work at three weeks, so it is suggested that there is a change in the corrosion mechanism at three weeks and it is thought that in-situ testing could be useful to determine if this is the case.

In addition to refining the elemental composition of stainless steel, further work will be required to determine how well the proposed new stainless steel can withstand the neutron fluxes within the molten salt reactor environment.

It is also envisaged that it would be possible to pre-coat a sample of stainless steel with the required protective layer, this would hopefully prevent the formation of a mixed oxide layer as seen in three
week test, but it will require refining the composition of the coating. The coating would need to adhere well to the surface and also be impervious to the salt as this would hopefully prevent corrosion of the bulk.