HIGH TEMPERATURE CORROSION OF NICKEL ALLOYS BY MOLTEN CALCIUM CHLORIDE IN AN OXIDISING ENVIRONMENT

Roger Barnett (TWI), United Kingdom (roger.barnett@twi.co.uk)
Mike Gittos (TWI), United Kingdom (mike.gittos@twi.co.uk)

ABSTRACT

A series of nickel alloys was submerged in molten calcium chloride (a molten salt proposed for and used in the nuclear industry for a variety of applications), at 850°C for 72 hours under an oxidising environment. The samples were analysed in detail, in order to determine their corrosion behaviour and suitability for use under these conditions. 310 stainless steel was used as a reference material.

Extensive corrosion occurred and the observed attack on the metal substrates was general and massive with corrosion rates ranging from 1.17mm/year, for Haynes 214, to 13.3mm/year, for 310 stainless steel. All materials showed selective leaching of chromium from the samples but the oxide layer formed was not protective, spalling away easily. The severity of the attack was not immediately visible from the corrosion rate alone: samples showed a friable scale on the surface and deep penetration of the attack beneath, up to 0.63mm for 310 stainless steel. In some cases, the attack was clearly intergranular with chromium being depleted along the grain boundaries, whereas in others, the attack was more general.

No simple correlation between alloying elements and corrosion rate was apparent, with additions of aluminium and silicon appearing to have little or no protective effect. Alloys 600 and Haynes HR-160 showed promise, with relatively low corrosion rates and penetration depths.
1. Introduction

In recent years, molten salts have once again increased in importance for use in the nuclear industry. Although molten chlorides are not often used directly in reactors or cooling systems, due to the difficulty involved in isotope separation, they are finding increasing use and being proposed for use in processing and reprocessing of radioactive material. Both pure salts and eutectic mixtures, with or without the addition of their counterpart oxides, are relevant to these applications. This is particularly true in the case of reprocessing of oxides and reprocessing of radioactive materials into their metallic form, including uranium, MOX and plutonium\(^1\).\(^2\).

Although there is extensive literature dealing with corrosion of metals in molten salts, pure molten chlorides have not been studied in as much detail, particularly not calcium chloride. Only a few corrosion experiments have been conducted in pure, molten CaCl\(_2\). Any materials utilised with this molten salt must not only have good mechanical properties at high temperature (CaCl\(_2\) melts at 778°C), but must have sufficient corrosion resistance to withstand the aggressive environment. The extent of attack is lower under argon than when oxygen is present, but this does not take into account possible contamination by oxygen, production of oxygen during any processes in the calcium chloride or the effect of leakage of molten salt into an air environment. The salt is also extremely hygroscopic and dissolved moisture can have significant consequences\(^3\). Consideration of this is important, not only for maintaining vessel integrity but also for preventing contamination of any products dissolved in the molten salt.

In general, molten chlorides attack steels very rapidly with preferential attack of the carbides. Selective losses of Cr, Fe and Co are observed in both steels and Ni-Cr-Fe alloys. Nickel alloys decrease in resistance as oxygen partial pressure increases. This poses a problem in a salt exposed to air. Studies by Jackson and LaChance, on alloys in NaCl-KCl-BaCl\(_2\) partial pressure increases, indicated that intergranular attack was more significant than metal loss and that, in general, reducing the grain size, or reducing the carbon content, led to increased resistance to intergranular attack\(^4\). Lai et al. conducted similar studies in an NaCl bath at 840°C, with the surprising result that some nickel alloys (600 and 601) were more severely attacked than stainless steels, such as 304 or 310. No simple correlation was found between alloying elements and corrosion rate\(^5\).

Studies by Cho et al on superalloys in LiCl at 650-850°C\(^6\), showed that the addition of at least 8% chromium to an alloy led to the formation of a protective LiCrO\(_2\) film. However, the addition of Li\(_2\)O to the molten salt led to accelerated corrosion and the basic fluxing of the protective Cr\(_2\)O\(_3\) scale by Li\(_2\)O. Fe-Cr-Ni alloys experienced greater corrosion with increased Cr content. Subsequent work, by the same authors, showed marked differences in corrosion rate and products between different alloys with Alloy 713 performing the best. Cr\(_2\)O\(_3\) was the common corrosion product, in all cases, with various other mixed oxides with a spinel structure, e.g., NiCr\(_2\)O\(_4\)\(^7\).

Work carried out by McLaughlin et al indicated that, in a CaCl\(_2\)-CaO environment, the projected lifetimes of nickel alloys were low. A porous surface was formed on Alloy 601 by the molten salt and intergranular attack was observed in Alloy 617. Both cases showed a selective loss of chromium, iron and cobalt and relative enrichment of nickel, molybdenum and copper. The average corrosion rates were in the region of 10-15mg/cm\(^2\)-h, with all metallic coupons completely chlorinated within the first 8 hour exposure period\(^8\).

Data from other cells, utilising calcium chloride for metal production, indicate that the materials are not only exposed to the CaCl\(_2\) or CaCl\(_2\)-CaO molten salt, but also to HCl and carbon monoxide at temperatures of 850°C or above\(^9\), dependent on the process utilised. The high solubility of CaO in CaCl\(_2\) means that it is difficult to entirely remove oxygen from the system. Contamination of metals and alloys by minor elements and alloying additions dissolved in the salt is also a potentially serious issue\(^10\),\(^11\), making the analysis of any corrosion products doubly important. 310 stainless steel has been utilised as a crucible in previous applications (under argon), with some observed corrosion but without cracking or other failure. It was, thus, selected as a reference material for this work\(^9\). It was not expected to resist the environment well.

2. Experimental
A series of alumina crucibles with a zirconia-glazed inner surface (Almath) was ultrasonically cleaned and degreased in acetone. After cutting and preparation, the corrosion coupons were cleaned with ethanol and then ultrasonically degreased with acetone, before being placed in said crucibles. In order to remove the majority of moisture from the system, prior to melting, calcium chloride was thermally dried in a multi-step process. 200g samples of calcium chloride (Sigma Aldrich) were placed in borosilicate glass trays in a muffle furnace (Vecstar PF4) heated to 60°C. The furnace was then heated at 1°C/min, until it reached 200°C. This temperature was held for 24 hours, prior to heating to 400°C. The salt was held at this temperature, for a minimum of 72 hours, before extraction.

The glazed alumina crucibles containing the metal corrosion coupons were charged with hot (400°C) salt. In order to ensure that the molten calcium chloride would entirely cover the coupons, when molten, the crucibles used were at least twice as high as the coupons. The filled crucibles were immediately placed in a secondary furnace at 400°C surrounded by aluminosilicate blocks with appropriate gaps to allow circulation. The entire furnace was placed under extraction, allowing free circulation of air. The temperature was maintained at 400°C for a further 24 hours to remove as much moisture as possible, before heating to 850°C at 1.5°C/min, in order to melt the calcium chloride. This temperature was held for 72 hours before cooling to 1.5°C/min to 300°C. The calcium chloride solidified around the coupons, protecting them and preventing further spallation of corrosion scale. A fresh crucible was used for each corrosion coupon, due to the attack observed on the crucible exterior after the first test run.

After extraction of the crucible, the coupons were extracted using gently flowing warm water to dissolve the salt and allow removal of the coupon, without significant losses of the friable corrosion scale.

A series of these coupons was soaked in water at 40°C for 2 hours, in order to dissolve any remaining salt but keep the corrosion scale intact, if at all possible. These were then mounted in EpoFix cold-set resin (Struers) and polished to a 0.25 micron finish on a plane perpendicular to the coupon surface. This was followed by examination with a FEG scanning electron microscope (LEO 1550) equipped with elemental mapping by energy-dispersive X-ray microanalysis. It should be noted that chlorine was detected in these scans, but the distribution and intensity of the chlorine correlated exactly with those for calcium (no other chlorine-containing phases were detected) and thus, for clarity, only the calcium trace is included.

In order to determine the loss of metal during corrosion, a second series of coupons was cleaned in accordance with ASTM G1-03. This involved gentle abrasion with a non-metallic brush followed by ultrasonic cleaning in water at 40°C. The coupons were then placed in an acid cleaning solution (80% water, 15% nitric acid, 5% hydrofluoric acid) for 2 minutes to remove any last traces of scale, before rinsing in water, drying and weighing. This cleaning procedure was duplicated for a third set of coupons that had not been exposed to molten salt, in order to establish that this method of cleaning did not lead to significant metal loss, only the removal of the scale.

3. Results and Discussion

3.1 General

After extraction from the salt and washing, all coupons were heavily corroded and covered in a layer of scale up to 0.5mm thick. Figure 1 shows an example of this: a 310 stainless steel coupon with a thick oxide layer on the surface. The corrosion scale was generally friable and did not normally adhere well to the coupon surface, although some small patches adhered strongly. The zirconia-glazed alumina inner of the crucible remained intact throughout the experiment. However, the unglazed alumina outside of the crucible suffered heavy attack beneath a fluffy white deposit on the surface. Figure 2 shows an example of a crucible after gentle washing with water to remove the deposit. This region of the crucible was not in direct contact with either the salt or the corrosion coupon. A green tidemark was also visible around the edge of the salt, after solidification, most likely corresponding to chromium oxide.

3.2 Corrosion Rate

Table 2 shows the calculated corrosion rates for each of the tested alloys, based on the weight loss after removal of the scale (following the above cleaning procedure) and the surface areas of the original coupons. The rates show a surprising variation in resistance to the molten salt environment. The most affected substrate (310 stainless steel) experienced corrosion rates over 10 times greater than those of the least affected substrate, Haynes 214. When submerged in a hot molten salt, the weight loss of the specimen with time can be attributed to cracking and dissolution of any protective layer, leading to spallation from the base metal surface. The mass loss in each case would be a function not just of the rate of reaction but also of the structure and composition of the corrosion
products on the surface and their adhesion to the bulk. The green tidemark, present in each case, also indicated that some or all of the chromium-rich corrosion products are at least slightly soluble in the molten salt.

### 3.3 Corrosion Behaviour

Figures 3–9 show SEM images of the metallographic cross sections of the alloys corroded for 72h at 850°C in molten CaCl₂ under air. The magnifications of the images are different in each case, due to the vastly different attack depths. Table 3 shows the depths of penetration and the scale thickness, for each alloy, after extraction from the salt. The penetration depth in this case was considered to be the point at which the alloy composition and microstructure after attack by the molten salt were unchanged from the alloy composition and microstructure before attack (as determined by SEM analysis of mounted reference samples of the same alloys). The depth of attack is not immediately apparent from scanning electron microscopy or light microscopy alone, as this does not clearly show elemental depletion, particularly that of chromium.

Considering the 310 stainless steel tested as a reference, Figure 3 shows the extent of the corrosion and the various elements present. The corrosion is massive but general, with no apparent intergranular attack or formation of voids. The total attacked zone is almost 1.5mm thick after only 3 days of exposure. The corrosion scale was not strongly attached and was rich in chromium and oxygen, indicating that it was most likely composed of Cr₂O₃, with an outer layer of calcium oxide or a mixed calcium-chromium oxide. Virtually no nickel was observed in the corrosion scale and only minimal iron. The nickel and iron contents of the steel beneath were higher, relative to the bulk, but this is most likely due to the extreme depletion of chromium. Silicon-rich oxides formed in the steel, but neither these, nor any other phase, appeared to impede the rapid outward diffusion of chromium. Interestingly, the level of aluminium appeared to be similar in the bulk alloy and the scale, indicating that once it has oxidised to alumina, it remains in its original position.

The two alloys least resistant to the salt were Alloy 800HT, a traditional high temperature alloy, and Haynes HR-120. Elemental maps of the corroded surfaces are shown in Figures 4 and 5. In a similar vein to the 310 stainless steel, there was a large chromium-depleted zone in the bulk of the substrate with a chromium and calcium-rich scale. Small concentrations of iron were also present in the scale. Silicon oxides formed in the substrate but were not protective. The titanium in Alloy 800HT also oxidised but did not make the scale protective. The primary differences between these two alloys were the thickness of the scale and the depth of penetration. Alloy 800HT suffered severe intergranular attack, with chromium depleted from the grain boundaries, whereas, Haynes HR-120 suffered a general attack with the formation of voids and various surface flaws: pockets of calcium oxide were observed inside the substrate. These two materials were also those with the greatest degree of penetration (excluding the reference 310 stainless steel).

The attack on Haynes 188 was a factor of 2 less than that of Haynes HR-120 and elemental maps of the corroded surface are shown in Figure 6. Haynes 188 was attacked in a more intergranular fashion. Chromium was depleted from the surface (and an oxide scale, very rich in chromium, was formed) and voids were created below the scale surface. However, chromium depletion along grain boundaries was also clearly visible, and, indeed, extended deeper into the substrate than shown in Figure 6. The scale contained some cobalt and iron, indicating that the chromium was not protective. However, virtually no nickel was observed in the corrosion scale. Aluminium was not located preferentially in the scale but evenly distributed through substrate and scale. Penetration into the substrate was less than 100μm.

Haynes HR-160 was more resistant to the salt, with its elemental maps shown in Figure 7. The attack was general, with the same pattern of chromium depletion from the surface and a chromium-calcium rich scale. The relatively high concentration of silicon in the substrate (2.75%) led to the formation of silica beneath the surface of the substrate. Silica formed at the innermost edge of the chromium-depleted layer. As a relatively low partial pressure of oxygen is required, in order to form silica, it is suggested that the silicon oxidised first, without creating a protective layer. However, penetration into the substrate was still less than 100μm.

Haynes 214 was the most resistant of all the Haynes alloys and, indeed, the most resistant of all materials tested, in terms of mass loss. Elemental maps of a corroded Haynes 214 coupon are shown in Figure 8. The same pattern is shown with chromium depletion near the surface and a chromium-rich scale. However, the high concentration of aluminium (4.5%) in Haynes 214 appears to be protective. An alumina layer was formed near the surface which slowed down mass loss from the substrate. Little or no iron or cobalt can be observed in the corrosion scale. Although the mass loss from this alloy was lower than from any other, the depth of penetration was still high (200μm).
Alloy 600 showed resistance approximately equal to Haynes 214, with one of the lowest nominal corrosion rates observed. Chromium was depleted from the surface, as seen in Figure 9, in a similar manner to other tested samples. The scale spalled away too easily to observe a sample of it in cross-section. Silica formed within the substrate, with the extent of the silica-containing regions coinciding with the edge of the chromium-depleted area. Curiously, the relative concentrations of iron and nickel in the chromium-depleted zone were not significantly changed from that of the unaffected substrate. The concentration of cobalt in the chromium-depleted zone was also relatively unchanged.

All depths of corrosion are plotted in Figure 10.

4. Conclusions

The severity of the corrosion of the various alloys, after only three days exposure, indicated the extremely aggressive nature of CaCl$_2$ in an oxidising environment. All the samples displayed deep attack into the coupons that was not immediately obvious from a surface inspection. It should also be noted that the resulting attack appeared to be oxidation rather than chlorination (though chlorination might have accelerated the oxidation). As such, the importance of keeping oxygen out of the system by means of utilising inert gas sheaths was illustrated. Additionally, although the zirconia lining was not damaged, the alumina crucible was. Alumina is normally resistant to a wide variety of corrosive environments, over a very large temperature range, and it raises concerns that it may not be usable in this environment. At this stage, the mechanism of attack has not been determined, but it is most likely to be due to the presence of calcium oxide. This compound could form calcium aluminate(s) by reaction with the alumina outer, or attack might occur from evaporated/condensed CaCl$_2$ and CaCl$_2$-CaO leaching impurities from the alumina and/or alumina binder and thus allowing small pieces to fragment away.

Several of the alloys used can immediately be ruled out as engineering alloys in this environment, even if there is little or no stress. The 310 stainless steel provided a useful baseline. Thus, although it has reasonable mechanical properties at the testing temperature, a sufficiently thick component would still lose up to 13mm/year, with the attack penetrating far beneath the surface, leading to potential cracking and failure. Alloy 800HT can also be ruled out, the high corrosion rate making it unsuitable for use.

All of the samples experienced massive chromium depletion at the surface, with the formation of a chromium-rich scale that spalled away and/or dissolved easily. This indicates that lower chromium contents may be beneficial in resisting the corrosive environment, though this may not be compatible with the requirement for high temperature strength and creep resistance. No other correlation between elemental composition and resistance to the environment was observed.

At high temperatures, the presence of aluminium and silicon in nickel alloys normally provides a measure of protection against a corrosive environment, by means of the formation of a corrosion-resistant scale. When exposed to the molten salt environment, this does not appear to be the case: aluminium and silicon oxidise beneath the surface, rather than forming a usefully protective scale. Those alloys that contained a higher level of aluminium or silicon were also not, in general, more resistant to the salt environment. It is believed that this is due to the relative concentrations of oxidising species and penetration beneath the sample surface. At deeper levels within the sample, the concentration of oxygen is low and only the most reactive species (aluminium and silicon) can oxidise, thus forming granules of alumina and silica beneath the surface.

Of the candidates tested, the best performers appeared to be Alloy 600 and Haynes HR-160. They showed a low mass loss, relative to other substrates, but this, alone, cannot be used as a guide to lifetime, due to the extreme depths of penetration observed in some instances. These materials also showed a relatively low depth of penetration into the substrate with general, rather than intergranular attack (which can create localised weakness and susceptibility to failure). This research provides a guideline to suitability, only, and cannot be used for the prediction of material lifetime without further data. However, the results do suggest that Alloy 600 and HR-160 are suitable for further study, in related environments, with or without the presence of air.

Acknowledgements

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Bibliography


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<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>Mo</th>
<th>Al</th>
<th>Mn</th>
<th>Co</th>
<th>Si</th>
<th>Other</th>
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<td>19.00-22.00</td>
<td>52*</td>
<td>24.00-26.00</td>
<td>-</td>
<td>-</td>
<td>2.00</td>
<td>-</td>
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<td>14.0-17.0</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
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<td>0.50</td>
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<td>19.0-23.0</td>
<td>-</td>
<td>0.15-0.60</td>
<td>1.50</td>
<td>-</td>
<td>1.00</td>
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<td>75*</td>
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* as balance single figures denote maxima except where indicated otherwise

**Table 1** – Specified compositions of the tested alloys (wt. %).

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated Corrosion rate (mm/year)</th>
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<tr>
<td>310 stainless steel</td>
<td>13.3</td>
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<tr>
<td>Alloy 600</td>
<td>1.22</td>
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<tr>
<td>Alloy 800HT</td>
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<td>Haynes HR-120</td>
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<td>Haynes HR-160</td>
<td>2.78</td>
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<td>Haynes 188</td>
<td>3.46</td>
</tr>
<tr>
<td>Haynes 214</td>
<td>1.17</td>
</tr>
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**Table 2** – Calculated corrosion rates of alloys in molten CaCl$_2$-CaO under air at 850°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Scale thickness (μm) if available</th>
<th>Depth of penetration (μm)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>630</td>
</tr>
<tr>
<td>Alloy 600</td>
<td>-</td>
<td>130</td>
</tr>
<tr>
<td>Alloy 800HT</td>
<td>108</td>
<td>300</td>
</tr>
<tr>
<td>Haynes HR-120</td>
<td>13</td>
<td>510</td>
</tr>
<tr>
<td>Haynes HR-160</td>
<td>16</td>
<td>67</td>
</tr>
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<td>80</td>
</tr>
<tr>
<td>Haynes 214</td>
<td>59</td>
<td>200</td>
</tr>
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**Table 3** – Extent of attack upon alloys in molten CaCl$_2$-CaO under air at 850°C. Penetration is considered to cease at the point where the alloy is unchanged from its original composition and microstructure.
Figure 1 Example of a 310 stainless steel corrosion coupon after 3 days exposure to the environment.

Figure 2 Example of an alumina crucible outer after 3 days exposure to the environment.

Figure 3 Elemental maps of a cross-section of 310 stainless steel corrosion coupon after exposure to the environment.
Figure 4 Elemental maps of a cross-section of Alloy 800HT corrosion coupon after exposure to the environment.

Figure 5 Elemental maps of a Haynes HR-120 corrosion coupon after exposure to the environment.

Figure 6 Elemental maps of a cross-section of Haynes 188 corrosion coupon after exposure to the environment.
Figure 7 Elementary maps of a Haynes HR-160 corrosion coupon after exposure to the environment.

Figure 8 Elementary maps of a Haynes 214 corrosion coupon after exposure to the environment.

Figure 9 Elementary maps of an Alloy 600 corrosion coupon after exposure to the environment.
Figure 11: All corrosion rates and attack depths.
Molten salts play an increasingly important role in the nuclear industry. Molten chlorides are finding increasing uses in the processing and recovering of radioactive material, with or without the addition of their counterparts oxides. This is particularly true in the reduction of oxides and reprocessing of radioactive materials into their metallic form, including uranium, MOX and plutonium.1,2

There is extensive literature dealing with the corrosion of metals in molten salts, but pure molten chlorides have not been studied in as much detail, particularly not calcium chloride. Corrosive attack is much lighter under argon, however contamination by oxygen, the production of oxygen during processes in the calcium chloride, and the effect of the leakage of molten salt into an oxidising environment must also be considered. The salt is also extremely hygroscopic and dissolved moisture can have serious consequences.2 The contamination of metals and alloys, by minor elements and alloying additions dissolved in the salt, is also a potentially serious issue, making the analysis of any corrosion products doubly important.2,1,7

This work provides corrosion data on a variety of engineering alloys under molten calcium chloride, for use in the nuclear industry and serves as a baseline for future work.

Experimental Method

Several batches of nominally anhydrous calcium chloride were subjected to further thermal drying. Those were loaded into a high-temperature furnace held at 1°C/min to 200°C, held for 24 hours, heated at 1°C/min to 400°C and held for a minimum of 72 hours.

Couples of various nickel-based engineering alloys were degassed with acetone and their masses and surface areas determined. 310 stainless steel was included, as a reference material, and was not expected to perform well. These couples were loaded into ZrO2-glazed alumina crucibles and then the crucibles were charged with hot dried calcium chloride. The crucibles were held at 400°C to remove any remaining moisture then heated to 850°C at 1.5°C/min in an apparatus that allowed free circulation of air, as shown in Figure 1. The crucibles containing molten salt were heated at this temperature for 72 hours then cooled, and the couples extracted from the solidified salt by gentle flowing of warm water to leave the corrosion scale intact. The couples were then sectioned, characterised by light and scanning electron microscopy with compositional analysis used as appropriate. The above process was repeated for other series of samples in order to determine the mass loss, after removal of corrosion products.

Results

All couples were heavily corroded, with thick scale layers on the surface. This scale was generally friable and poorly adherent to the substrate. The alumina exterior of the crucibles was also attacked, but the ZrO2-glazed inner remained intact. A green tidemark was present on the salt surface in each case, around the edges of the crucible, indicating that Cr-rich corrosion products are at least slightly soluble in the molten salt. Figures 1-7 show scanning electron micrographs and compositional maps of all material cross-sections.

Figure 1 - 310 stainless steel

In the reference 310 stainless steel, corrosion was extensive but general, with no apparent intergranular attack or void formation. The total attacked zone was almost 1.5mm deep and the poorly-attacked scale was most likely composed of 

\[
\text{Cr}_{2}O_{3},
\]

with an outer layer of CaO or a mixed Ca,Cr oxide. Virtually no Ni or Fe were observed in the corrosion scale. Si-rich oxides formed in the steel, but neither these, nor any other phase, appeared to impede the rapid outward diffusion of Cr. Al levels were similar in the bulk alloy and scale, indicating that, once oxidised to Al2O3, it remained in its original position.

Figure 2 - Alloy 600HT

The two least resistant alloys were Alloy 600HT and Haynes HR-120. Both showed a large Cr-depleted zone in the bulk alloy with Cr and Ca-rich scale, with some Fe. Again, the Ti and Ti (600HT only) oxides in the substrate were not protective. Alloy 800HT suffered severe intergranular attack, with Cr depleted from the grain boundaries, whereas, Haynes HR-120 suffered general attack with the formation of voids and various surface flaws; pockets of calcium oxide were observed inside the substrate.

Figure 3 - Haynes HR-120

Figure 4 - Haynes 188

Haynes 188 was attacked in a more intergranular fashion. Cr was depleted from the surface and along grain boundaries. A non-protective Cr-rich oxide scale formed, also containing Co and Fe, but no Ni. Voids formed below the scale surface. Al was not located preferentially in the scale but evenly distributed through both the substrate and the scale.

Figure 5 - Haynes HR-160

Haynes HR-160 was more resistant to the salt and showed general attack, Cr depletion from the surface and Cr-Ca rich scale. High levels of Si in the substrate (2.75%) led to the formation of SiO2 beneath the substrate surface and the formation of the Cr-depleted layer. As a relatively low partial pressure of oxygen is needed to form SiO2, the Si is likely to be oxidised first without creating a protective layer.

Figure 6 - Haynes 214

Haynes 214 was the most resistant of all materials tested, in terms of mass loss, again with Cr depletion near the surface and a Cr-rich scale. The high concentration of Al (4.5%) appeared to be protective. An Al2O3 layer formed near the surface slowing down mass loss from the substrate. Virtually no Fe or Cr was observed in the corrosion scale. However, the depth of penetration was still high (200μm).

Figure 7 - Alloy 600

Alloy 600 showed resistance similar to Haynes 214 and a low nominal corrosion rate, but the scale spalled away too easily to observe in cross-section. SiO2 formed within the substrate, with the extent of the SiO2 containing regions coinciding with the edge of the Cr-depleted area. The relative concentrations of Fe and Ni in the Cr-depleted zone were not significantly changed from that of the unaffected substrate. The concentration of Co in the Cr-depleted zone was also relatively unchanged.

Figure 8 - Scale thicknesses, depths of attack and corrosion rates for all materials

Conclusions

The severe attack of all materials (even alloys) indicates the extremely aggressive nature of CaCl2 in an oxidising environment, with the attack depth not obvious from surface inspection or mass change. The majority of the alloys tested can be ruled out as engineering alloys for prolonged use in this environment, even if little or no stress is present.

All materials experienced Cr depletion at the surface, with formation of non-protective Cr-rich-scale that spalled or dissolved easily. No direct correlation was observed between composition and resistance to attack. At high temperatures, Al and Si in nickel alloys normally protect against a corrosive environment, by formation of a protective corrosion-resistant scale. However, in this case Al and Si oxides beneath the surface. The alloys containing higher levels of Al or Si were not, in general, more resistant to the salt environment. It is believed that this is due to the relative concentrations of oxidising species and penetration beneath the sample surface. Deeper within the sample, the concentration of oxygen is low and only the most reactive species can oxidise, thus forming granules of Al2O3 and SiO2 beneath the surface.

The best performers are Alloy 600 and Haynes HR-160, showing relatively low mass losses and a relatively low depth of penetration. Attack was also general, rather than intergranular, which can create localised weakness and susceptibility to failure. This research provides a guideline to suitability, only, and cannot be used for prediction of material lifetime without further data. The results do suggest that Alloy 600 and HR-160 are suitable for further study, in related environments, with or without the presence of air.

References


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