Mechanical properties of Ni-base superalloys in high temperature steam environments

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Abstract

The effects of environmental damages on the mechanical properties of Ni-base superalloys, Alloy 617 and Haynes 230, were evaluated for VHTR-HTSE applications. Tensile tests were carried out at room temperature after ageing at 900°C in vacuum, steam, and steam + 20 vol.% H₂ environments up to 3 000 h. Also, creep rupture test were performed in air, steam, and steam + 20 vol.% H₂ environments. The degradations such as oxidation, decarburisation, and redistribution of carbides were studied in view of the interaction of materials with the environment. During the long-term ageing at 900°C in vacuum, secondary phases such as M₂₃C₆ and M₆C were precipitated and coarsened, which caused increase in tensile strength and decrease in ductility. For the specimens aged in steam environments, surface and internal oxides acted as preferential sites for crack initiation and consequently, decreased the tensile and creep strength. Also, the formation of decarburisation region resulted in glide plane failure during tensile test and reduction in creep rupture life due to grain boundary migration and recrystallisation. During creep tests, tensile stress caused the crack and void formation in oxide layer. Consequently, fast diffusion of oxidant occurred and environmental damage were accelerated. Among the test conditions, such environmental damage was much severe in steam environments.

1. Introduction

The very-high-temperature gas-cooled reactor (VHTR) combined with high-temperature steam electrolysis (HTSE) could achieve the massive and economical hydrogen production without CO₂ emission [1]. To demonstrate the VHTR-HTSE system, structural integrity of intermediate heat exchanger (IHX), for heat transfer from helium coolant in VHTR to steam in HTSE, should be assured.

Wrought Ni-base superalloys such as Alloy 617 and Haynes 230 are candidate materials for IHX in VHTR-HTSE system utilising good corrosion resistance and mechanical properties at high temperature environments. During operation, these materials will be exposed to high temperature above 850°C, operating pressure about 7MPa, and corrosive condition such as steam environments. The environmental damage caused by such operational exposure would significantly degrade the mechanical properties of IHX materials. However, such studies are not sufficient for the candidate IHX materials, especially in steam environments. Thus, in this study, the effects of long-term exposure on environmental damage and mechanical properties were investigated.

2. Test materials and experimental procedure

Two commercial wrought Ni-base superalloys, Alloy 617 and Haynes 230 were used in this study. The chemical compositions of test materials were analysed by inductively coupled plasma (ICP) method and results are shown in Table 1.
To evaluate the environmental effects on room temperature tensile properties, small size plate type specimen with 0.5 mm in thickness and 5 mm in gauge length were aged in vacuum, steam, and steam + 20 vol.% H2 conditions at 900°C up to 3 000 h. After the specimens were aged in various environments, tensile test were performed at room temperature with 3×10⁻⁴/sec strain rate. The cylindrical specimen with 4 mm in diameter and 16 mm in gauge length was used for creep rupture test. The constant load creep rupture test were carried out in air, steam, and steam + 20 vol.% H2 environments.

The environmental damages and microstructures were investigated using scanning optical microscope (OM), electron microscope (SEM), electron probe micro analyzer (EPMA), and focused ion beam (FIB) equipped with SEM.

### Table 1: Chemical compositions of Alloy 617 and Haynes 230 (wt%)

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ti</th>
<th>Al</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
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<tr>
<td>Alloy 617</td>
<td>Bal.</td>
<td>21.6</td>
<td>1.14</td>
<td>0.10</td>
<td>0.50</td>
<td>0.05</td>
<td>0.35</td>
<td>1.50</td>
<td>11.8</td>
<td>8.92</td>
<td>-</td>
</tr>
<tr>
<td>Haynes 230</td>
<td>Bal.</td>
<td>21.5</td>
<td>2.94</td>
<td>0.10</td>
<td>0.38</td>
<td>0.46</td>
<td>-</td>
<td>0.29</td>
<td>0.36</td>
<td>1.09</td>
<td>13.08</td>
</tr>
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</table>

### 3. Results and discussions

#### 3.1 Environmental effects on room temperature tensile properties

Figure 1 shows the room temperature tensile strength and elongation after ageing in vacuum, steam, and steam + 20 vol.% H2 environments. When aged in vacuum condition, tensile strength increased and ductility decreased. However, both strength and ductility decreased when aged in steam and steam + 20 vol.% H2 environments. Except elongation of Alloy 617, addition of 20 vol.% H2 additions in steam environment further reduced of tensile strength and ductility for both alloys.

For the as-received specimen, mixture of ductile dimples and brittle facets formed at intra-granular M₆C carbides were present on the fracture surface (Figure 2). After ageing heat treatment in vacuum up to 3 000 h, secondary phases such as M₂₃C₆ and M₆C carbides were extensively precipitated and then coarsened in gain boundary and grain, especially for Haynes 230 (Figure 3). Consequently, brittle fracture increased due to inter and intra-granular carbides. The increase in secondary phase such as MC, M₆C, and M₂₃C₆ in Ni-base Alloys was known to enhance the strengthening and decrease the ductility [2]. Therefore, the observed increase in tensile strength and decrease in ductility for the specimen aged in vacuum (Figure 1) could be explained by the increase in precipitates during ageing.

Authors reported that environmental damages such as surface oxide layer, internal oxides, and decarburisation were more extensively formed in steam with and without hydrogen environments than in air [3]. Similar results were observed in this study as shown in Figure 4. For Alloy 617, the damage by environments, that is oxidation and decarburisation, was much severe than Haynes 230. On the other hand, the precipitation of carbides was more extensive in the matrix, while the damage by environment was less significant for Haynes 230.

As shown in Figure 5, for Alloy 617, the surface oxide layer was broken in brittle manner, and internal Al₂O₃ oxides provided preferential path for cracking. Consequently, inter-granular cleavage fracture surface were observed until glide plane fracture happened in decarburisation region below. When the grain boundary was fully dissolved, it was reported that the glide plane fracture would be promoted rather than dimple formation [4]. It seems that the contribution of surface and internal oxides to the loss of ductility was greater than that of decarburisation zone to large ductility. As a result, it seems that surface and internal oxide decreased the tensile strength and ductility simultaneously for Alloy 617 aged in steam environments.
Figure 1: Tensile property changes after vacuum ageing and corrosion at 900 °C in steam and steam + 20vol.% H₂ environments up to 3 000 h: (a), (b) Alloy 617 and (c), (d) Haynes 230.

(a) (b)

(c) (d)

Figure 2: The fracture surfaces of as-received tensile specimen of Alloy 617.

In case of Haynes 230, the size of the broken surface oxide and glide fracture region were smaller than Alloy 617, but partially brittle fracture surface were observed at W-rich M₆C carbide regions. Similar to Alloy 617, the decrease in tensile strength and ductility could be related to the oxidation and decarburisation during ageing in steam environments. In addition, the presence of W-rich carbide below the oxide layer would have contributed further reduction in ductility for longer ageing time (Figure 1).
Figure 3: Microstructures and fracture surfaces of tensile specimen of Alloy 617 aged in vacuum at 900°C after 3000 h: a) cross-section, and b) tensile fracture surface.

Figure 4: Cross sectional microstructures corroded in steam + 20vol.% H₂ for 3000 h at 900°C: (a) Alloy 617 and (b) Haynes 230.

Figure 5: The fracture surfaces of tensile specimens corroded in steam + 20vol.% H₂ for 3000 h: (a) Alloy 617 and (b) Haynes 230.

The hydrogen additions in steam environments enhanced the environmental damage such as oxide and decarburisation as reported previously [3]. Consequently, further
degradation of tensile properties was expected for both Alloy 617 and Haynes 230. For Alloy 617, tensile strength was slightly reduced but ductility was higher in steam + 20 vol.% H₂ environments. The larger decarburisation zone would have contributed to higher ductility. However, in case of Haynes 230, both strength and ductility decreased in steam + 20 vol.% H₂ environments. Unlike Alloy 617, decarburisation region of Haynes 230 contained the trans-granular M₆C carbides which disrupted the glide plane fracture and therefore recovery of ductility by larger decarburisation zone was not observed.

3.2 Environmental effects on creep rupture strength

Figure 6 shows the creep rupture life of Alloy 617 and Haynes 230 in various environments. In general, the creep rupture life of both alloys is higher in air than in steam environments. Also, hydrogen additions in steam decreased the creep rupture life for Haynes 230. However, there is no significant effect of hydrogen addition on creep rupture life of Alloy 617.

Figures 7 and 8 show the OM and SEM photos of creep tested specimens showing the carbide redistribution and voids on grain boundary. The creep rupture process was well explained in the literature [5]. First, grain boundary carbides migrated from grain boundaries which are under compressive stress to those that are under tensile stress, which resulted in rearranged grain boundary carbides in perpendicular direction to tensile axis (Figures 7 (a) and 8 (a)). Then, grain boundary migrations occurred at carbide free region and then creep void are initiated. Finally, recrystallisation occurred, which accelerated the creep deformation by breaking up the grains.

These creep deformation mechanisms would be affected by the environmental damage occurred in various environments used in this study. As shown in Figures 7 (b) and 8 (b), oxide layer is broken by tensile load and initiated the surface crack. Then, inter-granular Al₂O₃ provide the preferential sites for surface crack propagation [10]. Eventually, propagation of surface crack would join with internal cracks emanated from the creep voids, resulting in accelerated creep failure. As mentioned previously, the environmental damage was greater in steam environments compared to in air, therefore creep rupture would be accelerated in steam environments (Figure 6).

Figure 6: The creep rupture life in various environments: (a) Alloy 617 and (b) Haynes 230

To quantify the environmental damage in various environments, oxide thickness and decarburisation depth were measured and plotted (Figure 9). In general, surface oxide thickness and decarburisation depth were larger in the creep tested specimens compared to isothermal tested specimens. Also, larger oxide layer size and decarburisation depth in steam environments were in good agreement with the shorter creep rupture life of Alloy 617 in such environments. The same relationship was also observed for Haynes 230.
As shown in Figure 10, void and surface cracks were formed in surface oxide layer under loading condition. According to the Kofstad [6], porosity of microchannel formed in oxide layer would permit the inward transport of oxidants. Therefore the fast transport of oxidant through microchannel increased the oxide growth rate in steam environments. Also, gas phase mass transport through void could occur by dissociative transport of $\text{H}_2\text{O}$ across voids in wet oxygen conditions such as $\text{H}_2\text{O}$ containing environments and therefore oxide growth rate was faster steam environments as previously reported [3,7,8].

Figure 7: Microstructures of ruptured Alloy 617 under 40MPa at 900°C in steam environment: (a) carbide redistribution, (b) environmental surface damage and cracks

Figure 8: Microstructures of ruptured Haynes 230 under 40MPa at 900°C in steam + 20vol.% $\text{H}_2$ environment: (a) carbide redistribution, (b) environmental surface damage and cracks

Figure 9: Quantifications of (a) surface oxide layer thickness and (b) decarburisation depth after isothermal corrosion test and creep rupture test for Alloy 617
The larger decarburisation depth would also accelerate the creep rupture as grain boundary carbide was known to suppress the grain boundary migration. As in the case of oxide thickness, decarburisation depth was greater under tensile loading and in steam environments (Figure 9). Beneath the surface oxide layer, Cr concentrations were depleted due to Cr-rich surface oxide formations and consequently, Cr-rich M\(_{23}C_6\) carbides were dissolved. Therefore, decarburisation depth would be proportional to the thickness of surface oxide layer. Also as previously reported [3], fine grained oxide layer were formed in steam environments (or low P\(_O_2\) condition), then substantial inward diffusion of water vapour would occur through increased grain boundary [9]. Thus, decarburisation was accelerated in steam environments, which in turn decreased the creep resistance.

4. Conclusions

The effects of environmental degradations on mechanical properties were investigated for Alloy 617 and Hynes 230. Based on the experiments and analysis, the following conclusions were drawn.

Long-term ageing at 900°C in vacuum caused the precipitation and coarsening of secondary phase such as M\(_{23}C_6\) and M\(_6C\), which caused increase in tensile strength and decrease in ductility. However, for the specimens aged in steam environments, surface and internal oxide as well as decarburisation region were formed along with secondary phases. The contribution of surface and internal oxides to the loss of ductility was greater than that of decarburisation zone to large ductility. As a result, tensile strength and ductility decreased simultaneously for specimens aged in steam environments.

In general, the creep rupture life of Alloy 617 and Haynes 230 was higher in air than in steam environments. Also, hydrogen additions in steam decreased the creep rupture life for Haynes 230. However, there is no significant effect of hydrogen addition on creep rupture life of Alloy 617. For both alloys, larger oxide layer size and decarburisation depth in steam environments were in good agreement with the shorter creep rupture life in such environments. Also, the surface oxide thickness and decarburisation depth were larger in the creep tested specimens compared to isothermal tested specimens.

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