Phase stability and segregation in Alloy 22 base metal and weldments

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ORD-FY04-015: Phase Stability and Segregation in Alloy 22 Base Metal and Weldments

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January 18, 2007
Desert Research Institute, Reno, NV
Task Overview:

Subtask 1: *Microstructural Characterization of Phase Stability and Variability in Alloy 22.*
Develop an improved understanding of Alloy 22 and the extent to which compositional and microstructural variations are present in otherwise “nominal” as-procured material.

Subtask 2: *Electrochemical Methods to Detect Susceptibility of Alloy 22 to Localized Corrosion.*
Study the influence that compositional and microstructural variations have on the corrosion performance of Alloy 22.
Subtask 1: Microstructural Characterization of Phase Stability and Variability in Alloy 22

**Issue 1.1** Characterize the as-fabricated Alloy-22 base metal.
*Optical microscopy, SEM, TEM, and X-ray diffraction*

**Issue 1.2** Characterize Alloy-22 welds.
*Optical microscopy, SEM, TEM, and X-ray diffraction*

**Issue 1.3** Long-term metallurgical stability: Cr-Mo depletion and Long Range Ordering.
*Determine how element depletion occurs adjacent to the grain boundary, and identify time and temperature relationship for diffusional transport processes. LRO study is on hold.*

**Issue 1.4** Segregation of sulfur and phosphorous
*Welded samples.*
Mill-Annealed Microstructure
Precipitation Formation

Example: 750°C for 100 hrs

100 hrs @ 650 °C
Prediction of the very-long term corrosion performance necessitates an estimation of the pace of atomic transport, i.e., the diffusivity.

This can be estimated from thermodynamic parameters, or measured directly.

Direct measurement is the most reliable, but will require a long-duration, directed study.

We have performed some preliminary measurements.
Linear Multicomponent Diffusion

A method to characterize the multicomponent diffusion from experimental data with a high degree of scattering was developed.
Diffusivity Matrix Evaluation Method

Experimental Data

- Raw Data
- Data Pretreatment
  - Concentration Profile
  - Genetic Algorithm
    - Tentative \([r]\)
      - B.F.G.S.
        - \([r]\) → \([D]\)

Cauchy/Solver

\([r]^A\) → \([r]^B\) → \([r]^C\) → \([r]^D\)

\([r]\) → \([D]\)
Linear Multicomponent Diffusion Results

\[
\begin{bmatrix}
D_{N Ni}^{Mo} & D_{N Ni}^{Mo} \\
D_{C Cr}^{Mo} & D_{C Cr}^{Mo}
\end{bmatrix}_{1215[K]} = \begin{bmatrix} 4.06 & 0.68 \\ -1.87 & 1.70 \end{bmatrix} \pm \begin{bmatrix} 0.46 & 0.40 \\ 0.42 & 0.36 \end{bmatrix} \cdot 10^{-10} \frac{cm^2}{s}
\]

\[
\begin{bmatrix}
D_{N Ni}^{Mo} & D_{NiCr}^{Mo} \\
D_{C Cr}^{Mo} & D_{C Cr}^{Mo}
\end{bmatrix}_{1195[K]} = \begin{bmatrix} 2.81 & 0.25 \\ -1.17 & 1.59 \end{bmatrix} \pm \begin{bmatrix} 0.13 & 0.11 \\ 0.14 & 0.10 \end{bmatrix} \cdot 10^{-10} \frac{cm^2}{s}
\]
Experimental Uncertainties

The uncertainty in the Diffusion parameters is reflected in the range of probable results.
Temperature Dependence of Diffusivity

Arrhenius plot multicomponent diffusion

Experimentally-Measured Data (2 temperatures)

High Temp Repository Model

Low Temp Repository Model

\[ \ln |D_{ij}| \text{[cm}^2\text{s}] \]

\[ \ln \frac{1000}{(T[K])} \]
D. Turnbull, in Atom Movements, ASM, Cleveland, (1951) p.129.
Phase Stability Model

Experimental observations of second phase growth (above 630 °C)

Experimental thermodynamic and mobility data (bulk diffusion only)

Microstructural Stability Model

The stability model’s predictions are based on experimental data that were derived at much higher temperatures than the repository operates at.

It was assumed that the high-temperature transformation mechanisms were the same as the lower expected repository conditions.

Assumption 5.2 in Wong, F., Aging and Phase Stability of Waste Package Outer Barrier. 2004(ANL-EBS-MD-000002 REV 02), p.5-1.
Subtask 2: *Electrochemical Methods to Detect Susceptibility of Alloy 22 to Localized Corrosion*

**Issue 2.1** Develop an EPR test solution and Cr depletion test procedure.

\[ 1M \text{H}_2\text{SO}_4 + 0.5M \text{NaCl} + 0.01M \text{KSCN} \text{ solution at } 300^\circ\text{C}. \]

**Issue 2.2** Develop an electrochemical test solution and Mo segregation test procedure.

\[ 2M \text{HCl} + 0.01M \text{KSCN} \text{ solution at } 60^\circ\text{C}. \]

**Issue 2.3** Study the effect of precipitation of secondary phases on the corrosion resistance of Alloy-22.

*Chemical weight loss (ASTM-G-28) and DL-EPR tests of heat treated samples (base metal and welds). DL-EPR tests will be done under various conditions. These will assess susceptibility of Nickel-based, Chromium-rich alloys towards intergranular corrosion.*
Cyclic polarization plots for each of 4 conds. (Example: Sample B-(Batch 1)

10% NaCl+H_2SO_4 (pH:1-2), 60°C.

Parameters
Initial E (V) = -0.213 vs. Eref
Apex E (V) = 1.4 vs. Eref
Final E (V) = 0.250 vs. Eref
Forward scan (mV/sec) = 0.1667
Reverse scan (mV/sec) = 0.1667
Apex I (mA/cm^2) = 5
Repeatability of DL-EPR Tests

Repeatability test on the same sample 2-B (Mill Annealed) using the same sample, test conditions, test parameters for checking the setup repeatability.
Chemical Weight Loss Tests (Preliminary)

Mill Annealed Samples with no macroscopic pitting

![Graph showing corrosion rate vs. temperature for various data sets and methods.]

- Our Data, Method A
- Our Data, Method B
- Rebak & Crook (A)
- Rebak & Crook (B)
- Rebak, Edgecombe, & Lian et al. (A)
- Agarwal & Corbett (A)
- Agarwal & Corbett (B)
Preliminary Conclusions:

• Banded formations of precipitates appear to grow from “incomplete” mill annealing, designed to homogenize the microstructure and composition.

• Both grain boundaries and twin boundaries may affect transport and phase stability, and warrant investigation.

• The mode of diffusion (bulk vs. interfacial) may be different at repository conditions. This can lead to a very large error when using transport data obtained at higher temperatures.

• The (limited) data gathered thus far indicate that chemical weight loss measurements are consistent with expectations of correlations between localized corrosion and GB precipitates.
Supplementary Slides
### Progress Metrics:

<table>
<thead>
<tr>
<th>Test Description</th>
<th>Planned</th>
<th>Completed</th>
<th>% Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Treatment Complete, (or Mill Annealed)</td>
<td>138</td>
<td>59</td>
<td>43%</td>
</tr>
<tr>
<td>Optical Image Capture Complete (Heat Treatment)</td>
<td>91</td>
<td>18</td>
<td>20%</td>
</tr>
<tr>
<td>Quantitative Metallography Complete</td>
<td>73</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>Chemical weight loss test (ASTM-G-28-A-B)</td>
<td>69</td>
<td>10</td>
<td>14%</td>
</tr>
<tr>
<td>EPR test (in chloride solutions)</td>
<td>66</td>
<td>8</td>
<td>12%</td>
</tr>
<tr>
<td>EPR test (For Cr depletion)</td>
<td>63</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>EPR test (for Mo depletion)</td>
<td>63</td>
<td>0</td>
<td>0%</td>
</tr>
</tbody>
</table>
EPR Test Apparatus
EPR Sample Holder

Steel Rod (Conducting)

PTFE Tube

PTFE

Sample

O-Ring
DL-EPR Indications of Localized corrosion

Localized Corrosion
RP < CP

NO Localized Corrosion
RP > CP
SEM/EDS of selected samples affected by Localized Corrosion
Example: 14-G after ASTM-G-28 B test @ 210 °C
Etched Grain Boundaries on Annealed Samples
(Grain boundary precipitates)
SEM/EDS of selected samples affected by Localized Corrosion
Example: 14-G after ASTM-G-28 B test
Fig. 4. Chemical diffusion coefficient in Fe–Cr alloys at different temperatures. Symbols are experimental data due to Carter\textsuperscript{24} (triangles), Heumann and Böhmer\textsuperscript{16} (squares), and Sulayev \textit{et al.}\textsuperscript{35} (circles). Solid lines are from our assessment.
Data down to ~630 °C

Precipitate Growth Experimental Data

Thermodynamic Database

Mobility Database

Christian
Precipitate Evolution Formulation, 1981

Kinetic Model

Anderson and Ågren Diffusion Formulation, 1992

TTT Calculated Diagrams

Microstructural Stability on Alloy 22

Exponential Dependence:

\[ f = 1 - \exp \left( C \exp \left( \frac{-C_2}{T} \right) \right) \cdot t^n \]

Compared with data to 700 °C

Does not consider g.b. diffusion or alternative path.

Thus additional model for microstructural evolution (and experimental data) to account diffusion mechanism at low temperatures are required.
Figure 94. Time to Form 1 and 5 vol % TCP Phase in C-22 Welds as a Function of Aging Temperature

\[ f = 1 - \exp \left[-\left(C_1 \exp \left[\frac{-C_2}{T}\right] \right) \cdot t^n \right] \]
<table>
<thead>
<tr>
<th>Heat treatment given</th>
<th>Corrosion rate (in mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-A (Mill annealed)</td>
<td>384.786 (9.773mm/yr)</td>
</tr>
<tr>
<td></td>
<td>Pitting was seen.</td>
</tr>
<tr>
<td>9-B (Mill annealed)</td>
<td>10.01 (0.254mm/yr)</td>
</tr>
<tr>
<td></td>
<td>No pitting seen.</td>
</tr>
<tr>
<td>14-A (Sensitized at 650°C)</td>
<td>527.521 (13.39mm/yr)</td>
</tr>
<tr>
<td></td>
<td>Pitting was seen.</td>
</tr>
<tr>
<td>14-G (Sensitized at 700°C)</td>
<td>688.33 (17.48mm/yr)</td>
</tr>
<tr>
<td></td>
<td>Pitting was seen.</td>
</tr>
</tbody>
</table>

### Corrosion Rates (Preliminary)

**(ASTM-G-28-Method A@ 210 °C)**

<table>
<thead>
<tr>
<th>Heat treatment given</th>
<th>Corrosion rate (in mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-A (Mill annealed)</td>
<td>21.3564 (0.542mm/yr) <em>(Localized corrosion was at the interface between the glass and the metal)</em>.</td>
</tr>
<tr>
<td>9-B (Mill annealed)</td>
<td>5.3319mpy (0.1354mm/yr) <em>(No pitting was seen)</em></td>
</tr>
<tr>
<td>9-A (Mill annealed)</td>
<td>27.821mpy(0.7066mm/yr) <em>(Pitting was seen due to a preexisting pit)</em></td>
</tr>
<tr>
<td>14-G (Sensitized at 700°C)</td>
<td><strong>8.086 (0.205mm/yr)</strong> <em>(Due to a preexisting pit that aggravated corrosion)</em></td>
</tr>
<tr>
<td>14-A (Sensitized at 650°C)</td>
<td>137.97 mpy (3.44 mm/yr) <em>(Due to a preexisting pit that aggravated corrosion)</em></td>
</tr>
</tbody>
</table>