THE INFLUENCE OF STRENGTHENING PRECIPITATE MORPHOLOGY ON HYDROGEN ENVIRONMENT-ASSISTED CRACKING (HEAC) IN MONEL K-500

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Abstract
Monel K-500 is a Ni-Cu superalloy prone to hydrogen environment-assisted cracking (HEAC) despite an excellent combination of corrosion resistance, strength, and fracture toughness. However, lot-to-lot variations in metallurgical features and hydrogen-metal interactions have been shown to influence HEAC susceptibility of peak-aged Monel K-500. This study investigates the role of strengthening precipitate morphology on the HEAC susceptibility of Monel K-500 by systematically varying heat treatments to produce strengthening precipitate (γ' (Ni₃Al)) sizes that result in distinct global slip behavior (i.e. Orowan looping vs. particle shearing). HEAC susceptibility is initially assessed through slow-rising stress intensity testing of non-aged and over-aged Monel K-500 immersed in 0.6 M NaCl while under cathodic polarization. Results indicate that both non-aged and over-aged alloys are not susceptible to HEAC when polarized to potentials more positive than -1000 mV\text{SCE}. Both conditions demonstrate increased susceptibility at -1200 mV\text{SCE}, though crack growth rates are accelerated for the over-aged alloy. Speculatively, differences in local crack-tip deformation interactions with hydrogen or impurity segregation of sulfur to grain boundaries may contribute to the observed variation in HEAC susceptibility, though additional testing as well as high-fidelity FIB-TEM investigations are needed to fully evaluate these possibilities.

Introduction
Nickel-based superalloys exhibit exceptional mechanical properties and excellent resistance to chemical degradation\cite{1,2}. However, despite this inherent resistance to chemical attack, Ni-based superalloys have proven to be susceptible to hydrogen environment-assisted cracking (HEAC) when stressed in aggressive hydrogen-producing environments\cite{2-4}.

The deleterious effects of hydrogen on the mechanical properties of structural metals have been widely investigated in the literature\cite{5-7}. Four primary mechanisms for hydrogen damage have significant experimental and theoretical support: (1) hydrogen-enhanced decohesion (HEDE), hydrogen-enhanced localized plasticity (HELP), (3) adsorption-induced dislocation emission (AIDE), and (4) the formation of a brittle hydride in susceptible alloy systems\cite{5-9}.

Though the relative contributions of the H-damage mechanisms to HEAC remain under debate, the reduction in service life for structural components due to HEAC is well established\cite{10}. One example is that of the long-time (10 years) service failures of Monel K-500 threaded bolts that have been used in offshore oil platforms and submarines\cite{2,10,11}. These bolts are often used to connect steel components, which require cathodic polarization for protection against corrosion. The immersion of these components in seawater, combined with the exposure to
cathodic polarization, results in the production and uptake of hydrogen. The ingress of hydrogen causes premature failure accompanied by a transition in fracture mode from ductile microvoid coalescence to brittle intergranular failure\(^6\)–\(^8\).

Differences in HEAC susceptibility in a single alloy system are typically attributed to variations in environment, component loading, and/or microstructure. For Monel K-500, an initial study\(^2\) evaluated the former two, while recent research\(^1\) investigated the role of microstructural variation. Specifically, the authors evaluated features ranging from grain size and boundary character to hydrogen-metal interactions in five peak-aged lots of Monel K-500 obtained from various vendors. Despite the thorough nature of this work, limited correlations with HEAC susceptibility were found with the measured material properties, thereby suggesting that other microstructural influences, such as precipitate morphology, may dominate instead.

The objective of this study is to systematically evaluate the variation in HEAC behavior of Monel K-500 with changing strengthening precipitate morphologies. In this initial report, the ageing curve for the procured lot of Monel K-500 is established and four ageing times, representing various precipitate-dislocation interactions, are selected for evaluation via high-fidelity fracture mechanics testing. Specimens heat-treated to the non-aged and over-aged condition are tested in four environments of increasing severe hydrogen concentrations to quantify differences in HEAC susceptibility with ageing condition. Interpretations from this initial data set are discussed and a brief overview of future work is presented.

**Experimental Methods**

Monel K-500 is composed of an austenitic Ni-Cu solid solution matrix (\(\gamma\)) that is precipitation-hardened by the intermetallic \(\gamma'\) (Ni\(_2\)(Al,Ti) phase. These homogeneously distributed \(\gamma'\) precipitates are highly coherent, even after prolonged ageing times, with an ordered L1\(_2\) structure composed of Ni atoms at the faces and Al (or Ti) atoms on the corners of the unit cell\(^1\)\(^3\)–\(^1\)\(^5\). Due to the low misfit strain between the \(\gamma\) and \(\gamma'\) (<0.1%), the \(\gamma'\) precipitates form as spherical particles\(^1\)\(^4\). \(\gamma'\)-dislocation interactions are predominantly controlled by the size of the \(\gamma'\) precipitates, with a noted shift from dislocation cutting to Orowan looping as the particle radii increases\(^1\)\(^4\),\(^1\)\(^5\). A third phase, MC-type carbides (typically TiC), which form upon solidification, are widely spaced and heterogeneously distributed throughout the alloy. As such, their distribution does not change with ageing and they provide a minimal contribution to the strength of Monel K-500.

In this study, a single lot of Monel K-500 was procured from Vincent Metals (Minneapolis, MN) in the solution-annealed condition as 6 m-long, 1.6 cm-diameter bar stock. Elemental composition, shown in Table 1, was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) for bulk elemental analysis and glow discharge mass spectroscopy (GDMS) for trace element analysis.

<table>
<thead>
<tr>
<th>Ni</th>
<th>Cu</th>
<th>Al</th>
<th>Ti</th>
<th>Mn</th>
<th>Fe</th>
<th>Si</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>62.3</td>
<td>31.8</td>
<td>2.96</td>
<td>0.59</td>
<td>0.7</td>
<td>0.78</td>
<td>850</td>
<td>69</td>
<td>31</td>
</tr>
</tbody>
</table>

To establish the required heat treatments for producing the desired variations in \(\gamma'\) morphology, 12 cylindrical specimens were rough-cut from the bar to dimensions of 3.8 cm in length and 1.27 cm in diameter. These specimens were then solution annealed in a tube furnace at 1223 K for one hour, followed by a water quench, to ensure a \(\gamma'\)-free starting
condition prior to ageing. Individual specimens were then aged in a tube furnace at 923 K for times ranging from 0 (not aged) to 100 hours, followed by a water quench, with duplicates being aged for 0 hours and 2 hours to assess reproducibility of results. The specimens were then compressively stressed to 2% strain at Westmoreland Mechanical Testing and Research (Youngstown, PA) to determine yield strength and the Ramberg-Osgood flow constants (n, α). These constants were calculated from experimental true stress-true strain data obtained during compression testing through a best fit analysis to values predicted by the Ramberg-Osgood equation (Eqn. 1):

\[ \epsilon_T = \frac{\sigma_T}{E} + \alpha \left( \frac{\sigma_T}{\sigma_0} \right)^n \]  

(1)

Where \( \epsilon_T \) and \( \sigma_T \) are the true strain and stress, \( E \) is the modulus of elasticity, and \( \sigma_0 \) is the yield strength.

Cylindrical blanks were rough-cut to 10.2 cm in length and heat-treated to the desired age condition. Heat-treated specimens were then machined into single-edge notched tensile (SEN(T)) specimens with gauge sections of 12.5 mm in width (W) and 2.68 mm in thickness (B). A 200 ± 10 µm notch was machined in the center of the gauge section using electrical discharge machining (EDM). Specimens were machined such that the loading direction was parallel to the bar’s longitudinal axis with Mode I crack growth occurring in the radial direction. All specimens were fatigue precracked in laboratory air using a MTS 810 mechanical testing frame (Eden Prairie, MN) with the following protocol: (1) constant maximum load of 10 kN at \( \text{R}^a = 0.1 \) from the initial to notch to a notch plus crack length of 0.75 mm (ending \( K_{\text{max}} \approx 16.5 \text{ MPa}\sqrt{\text{m}} \)), (2) constant \( K_{\text{max}} = 16.5 \text{ MPa}\sqrt{\text{m}} \) at \( \text{R} = 0.1 \) from a notch plus crack length of 0.75 mm to 2.6 mm, and (3) constant \( R = 0.1 \) with \( K_{\text{max}} \) decreasing from 16.5 MPa\( \sqrt{\text{m}} \) to 13.5 MPa\( \sqrt{\text{m}} \) at a final notch plus crack length of 3 mm. This protocol was utilized so as to avoid the development of extensive plasticity in the remaining specimen ligament. Each specimen was loaded using clevis grips so as to allow for free rotation in compliance with K-solution boundary conditions.

Hydrogen environment-assisted cracking susceptibility was evaluated through slow-rising stress intensity (K) testing of fatigue-precracked specimens. Active crack length feedback coupled with software-controlled servo-hydraulic actuator displacement enabled fracture mechanics testing at a constant increasing elastic K rate (dK/dt) of 0.33 MPa√m/hr, which approximately corresponds to a constant grip extension rate of 2x10^{-9} m/s. Crack progression was monitored via the direct current potential difference (DCPD) method. Software developed by Fracture Technology Associates (Bethlehem, PA) automated current-polarity reversal for eliminating thermally-induced voltages, crack potential difference normalization via remote reference probes, and block-averaging of voltage data for noise minimization. Each potential measurement was converted to a crack length via Johnson’s equation. The minimum resolvable average crack extension, \( \Delta a \), for this technique is approximately 0.5 µm, based on the ability to resolve 0.1 µV changes in measured potential difference. Due to the volume of collected crack length and time data, these data were divided into bins of approximately 200-500 data points and averaged prior to analysis. Crack growth rates were determined using the incremental (n=3) polynomial method described in ASTM E647-13 Appendix X1. The effects of specimen plasticity are accounted for using a J-integral procedure to

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\( ^a \) The stress ratio (R) is defined as the ratio of the minimum applied load to the maximum applied load, i.e. \( \frac{P_{\text{min}}}{P_{\text{max}}} \).
calculate the total stress intensity, $K_J^{21}$. Remaining ligament plasticity was evaluated via analytical limit load solutions for an SEN(T) geometry which deforms according to the Ramberg-Osgood flow rule$^{21}$. False $da/dt$ were observed at low $K$ due to crack surface electrical contact enabled by the cathodic polarization-induced destabilization of the passive oxide film. A post-test analysis protocol described elsewhere was used for data correction$^2$.

Specimens were evaluated at room temperature in four testing environments: full immersion in dry nitrogen gas (RH < 5%) and aqueous 0.6 M NaCl solution with an applied potential of -850, -1000, and -1200 mV$_{\text{SCE}}$ (vs. saturated calomel). Previous testing suggests that the HEAC susceptibility in these environments are nil, mild, aggressive, and extreme, respectively$^{2,12}$. To immerse the specimen in the environment, the gauge section of the SEN(T) specimens was placed inside a 340 mL cylindrical Plexiglass cell. Dry nitrogen testing was completed by flowing high-purity $N_2$ into the environmental cell at a rate that maintained a measured relative humidity of less than 5% for the duration of the test. Immersion testing was completed by circulating 0.6 M non-deaerated NaCl solution from a 2L reservoir at ~40 mL/min. The desired applied potential, referenced to a saturated calomel electrode (SCE), was held constant by a potentiostat operating in floating ground mode (so as to avoid a ground loop). The SEN(T) specimen was grounded through grip attachment to the testing machine. A platinum-coated Nb mesh counter-electrode and the SCE were placed in the cell with the counter-electrode surrounding the specimen. The open circuit potential of the specimen was monitored for 1 hour prior to the start of testing, followed by the specimen being polarized to the selected test potential. To minimize the possibility of side-cracking, only a 1 mm window surrounding the Mode I crack path from the notch to an $a/W$ of 0.8 was exposed to solution; all other surfaces within the cell were masked with 3M Electroplating Tape 470 and a butyl rubber-based lacquer (Tolber Microxp-2000 Stop-off Lacquer). Upon final fracture, each specimen was sonicated in acetone and methanol for 15 minutes each, thoroughly rinsed with deionized water, dried, and then stored in a desiccator.

Fracture surfaces were imaged using a FEI Quanta 650 FEG scanning electron microscope (SEM) operated in secondary electron mode with an accelerating voltage ranging from 3-5 kV and a working distance between 9-11 mm.

**Results**

Measured yield strength as a function of ageing time is presented in Figure 1. From these data, the 0, 0.5, 5, and 50 hour ageing times at 923 K were selected for further study and are referred to herein as the non-aged, under-aged, peak-aged, and over-aged conditions, respectively. These conditions are identified by expected interactions between $\gamma'$ and dislocations; namely, a lack of $\gamma'$ resulting in wavy slip (non-aged), small precipitates resulting in planar slip via particle shearing (under-aged), and Orowan looping about larger $\gamma'$ producing wavy slip (over-aged)$^{15}$. The apex of the curve identifies the peak-aged condition where a mix of particle shearing and Orowan looping is expected to occur.
The da/dt versus $K_J$ data for the non-aged condition in the four test environments are shown in Figure 2. Testing conducted in dry $N_2$ (no applied potential) and 0.6 M NaCl solution at -850 and -1000 mV$_{SCE}$ show similar crack growth rates for the applied $K_J$, while the -1200 mV$_{SCE}$ results show increasingly larger crack growth rates as $K_J$ increases.

The da/dt versus $K_J$ data for the over-aged condition in the four test environments are shown in Figure 3. As was found for the non-aged condition, testing conducted in dry $N_2$ and 0.6 M NaCl solution at -850 and -1000 mV$_{SCE}$ show similar crack growth rates for a given applied $K_J$. However, the results for testing at -1200 mV$_{SCE}$ show substantially increased crack growth rates over the previous three environments.

**Discussion**

The crack growth rate versus total stress intensity data in Figures 2 and 3 demonstrate remarkable similarities in susceptibility between the non-aged and over-aged heat treatment conditions. The convergence of the -1000 mV$_{SCE}$, -850 mV$_{SCE}$, and dry $N_2$ testing results in both conditions indicates enhanced HEAC resistance relative to previously tested materials with more complicated multi-step aging processes$^{2,12,22}$. In particular, these results indicate the presence of an immunity potential near -1000 mV$_{SCE}$, which is approximately 100 mV more negative than the previously measured value (-900 to -840
mV$_{\text{SCE}}$)\textsuperscript{22}. Testing conducted at -1200 mV$_{\text{SCE}}$ demonstrated the onset of HEAC susceptibility, as shown by the increased crack growth rates relative to testing at more positive potentials. Notably, the over-aged material proceeded to crack at significantly elevated rates relative to the non-aged material for this applied potential, especially at low $K_J$.

These results provide an interesting contrast to previous HEAC susceptibility data measured for five lots of peak-aged Monel K-500\textsuperscript{12,22}. While the more negative immunity potential suggests enhanced HEAC resistance for both the non-aged and over-aged conditions, the mechanistic underpinnings behind this variation in susceptibility are unclear. Speculatively, the influence of a lower yield strength, and therefore increased ductility and toughness, may result in improved cracking resistance. It is generally accepted that HEAC resistance is inversely proportional to the yield strength of a material; this trend has been leveraged in the crafting of standards and other technical specifications\textsuperscript{23}. Mechanistically, this difference in yield strength between the non-aged/over-aged and the previously tested peak-aged Monel lots (~500 MPa vs. non-aged, ~200 MPa vs. over-aged) could give rise to variations in interactions between hydrogen and dislocations. For example, as the $\gamma'$ grows in size, the interaction of the precipitates with dislocations will change, resulting in global changes in slip morphology. Subsequent interactions with hydrogen could further modify the global slip. Critically, these changes in global slip may also result in changes to the localized slip morphology near the high-stress region of a crack-tip. Recent evidence suggests that hydrogen enhances the localized slip morphologies such that they reach a level of organization that is much greater than anticipated for the given applied stress\textsuperscript{24}. The interplay of these two sets of interactions and their role in determining HEAC susceptibility will be evaluated in future work.

Differences in crack growth rates versus total K for testing completed at -1200 mV$_{\text{SCE}}$ in the non-aged and over-aged conditions can be speculatively attributed to two factors. First, the possibility of differences in localized slip morphology cannot be ruled out, despite similarities in the global slip (both conditions have nominally wavy slip behavior) morphology. Second, the possible contribution of impurity segregation to grain boundaries, particularly sulfur, becomes increasingly likely with longer ageing time. The deleterious effect of sulfur on the strength of Ni-based alloys is well-known\textsuperscript{25,26}; as is the propensity for sulfur to enhance the effects of hydrogen via a synergistic embrittlement\textsuperscript{27,28}. Data provided by Mulford\textsuperscript{26} indicates that the selected ageing temperature (923 K) in this study resides near the point of maximum sulfur segregation to grain boundaries in Ni, suggesting that the over-aged material may be inherently more prone to subcritical crack growth than the non-aged material. This line of thought is directionally consistent with the results of the -1200 mV$_{\text{SCE}}$ testing, where the over-aged condition demonstrated enhanced HEAC susceptibility relative to the non-aged condition. Speculatively, sulfur may be preemptively embrittling the grain boundaries of the over-aged material, leading to reduced HEAC resistance. Further experiments are necessary to determine the concentration of sulfur segregated to the grain boundaries as a function of ageing time.

**Future/Ongoing Work**

Current efforts are focused on: (1) obtaining crack growth kinetics data for the under-aged and peak-aged conditions and (2) evaluating $\gamma'$ precipitate morphology and interactions between $\gamma'$ and dislocations as a function of applied heat treatment using transmission electron microscopy. These data will then provide the inputs to evaluate the ability of
current micromechanical modeling paradigms to correctly predict the effect of microstructural variation on HEAC susceptibility.

A parallel set of experiments are investigating the extent of sulfur segregation to grain boundaries as a function of ageing time at 923 K. Small pin specimens were heat treated to the conditions of the non-aged, under-aged, peak-aged, and over-aged materials detailed in this report and then electrochemically charged with hydrogen for 33 days at \(-1200 \text{ mV}_{\text{SCE}}\). These specimens will be in-situ fractured inside an Auger Electron Spectrometer so as to allow analysis of sulfur content along intergranular facets.

**Conclusions**

In this study, the ageing curve at 923 K for a procured lot of Monel K-500 was developed. Preliminary fracture mechanics testing of Monel K-500 specimens heat-treated to the non-aged and over-aged conditions were performed to quantify differences in HEAC susceptibility as a function of strengthening precipitate morphology. The following conclusions can be drawn from this initial report:

1. The systematic evaluation of yield strength as a function of ageing time at 923 K highlights the required heat treatments to achieve the non-aged, under-aged, peak-aged, and over-aged conditions.
2. Initial fracture mechanics testing suggest an immunity potential exists at approximately \(-1000 \text{ mV}_{\text{SCE}}\) for both the non-aged and over-aged specimens.
3. Both the non-aged and the over-aged conditions exhibit accelerated crack growth rates when tested at \(-1200 \text{ mV}_{\text{SCE}}\), though cracking is more severe for the over-aged material.
4. Speculatively, differences in localized deformation near the crack-tip or sulfur segregation to grain boundaries may contribute to the observed variation in HEAC susceptibility at \(-1200 \text{ mV}_{\text{SCE}}\). These possibilities will be investigated with additional testing and high-fidelity TEM-FIB and Auger electron spectroscopy experiments.

**References**


