GRAIN BOUNDARY CHEMISTRY
CONTRIBUTIONS TO INTERGRANULAR HOT CRACKING
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To cite this version:
R. Thompson, B. Radhakrishnan, D. Mayo. GRAIN BOUNDARY CHEMISTRY CONTRIBUTIONS TO INTERGRANULAR HOT CRACKING. Journal de Physique Colloques, 1988, 49 (C5), pp.C5-471-C5-479. <10.1051/jphyscol:1988559>. <jpa-00228056>

HAL Id: jpa-00228056
https://hal.archives-ouvertes.fr/jpa-00228056
Submitted on 1 Jan 1988

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ABSTRACT

This report presents recent findings concerning the role of intergranular chemistry in the mechanism of intergranular hot cracking IHC during welding. The IHC of the weld heat affected zone during welding has long been suspected of some relationship to residual elements. Until now, that relationship in nickel alloys had been lost due to the roles that bulk concentration, volume fraction of second phase, and heat treatment played in establishing the intergranular chemistry of the alloy. Experiments in this study correlated the IHC susceptibility with bulk sulfur and heat treatment. It is shown that increasing sulfur from 0.0008 to 0.009 weight percent caused a modest increase in IHC. However, heat treatment had a three fold greater effect on IHC than the sulfur range tested. It is postulated that, although an increase in bulk sulfur increases the intergranular sulfur level, heat treatment has a more potent effect on IHC through combined segregation and precipitation reactions. Auger spectroscopy, metallography, and IHC data are presented in defense of these arguments.

INTRODUCTION

Intergranular hot cracking (IHC) occurs during many processes and in many alloy systems. One form of IHC occurs in the base metal heat affected zone, next to the fusion zone, during welding. This form of IHC is often called microfissuring but will be referred to hereafter simply as IHC. It is this form of IHC in nickel alloy 718 which is the topic of this paper.

IHC next to the weld fusion zone is a complicated process which has been shown to be a function of the following:

- welding thermal cycle (unpublished work by A.C. Nunes, NASA-MSFC)
- residual stress cycle (unpublished work by A.C. Nunes, NASA-MSFC)
- grain size (1)
- heat treatment (2, 3, 4, 5, 6)
- volume fraction of second phase (7 and unpublished research by Thompson, Mayo and Radhakrishnan)
- grain boundary precipitation (11)
- constitution liquation of second phase (5, 8, 9, 10)
- grain boundary segregation (6, 12)

The present study considers the effects of grain boundary precipitation and grain boundary segregation on the IHC mechanism.

Sulfur had long been suspected of contributing to IHC in nickel alloys (2, 4, 6, 13, 14). Canonico et. al. (14) used Borland's (15) relative potency factor to show that sulfur should be much more potent than other elements in promoting IHC.
TABLE 1 (After Canonico (14))

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative Potency Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>244,000</td>
</tr>
<tr>
<td>B</td>
<td>22,700</td>
</tr>
<tr>
<td>P</td>
<td>6,430</td>
</tr>
<tr>
<td>C</td>
<td>300</td>
</tr>
</tbody>
</table>

These numbers are for binary nickel alloys and multiphase interactions such as reported by Owczarski (10) between carbides and borides in nickel alloys are expected to greatly offset relative potency factors. However, studies (2, 13) have indicated that high bulk sulfur can lead to increased IHC.

The effect of heat treatment on IHC has been studied by many authors (2, 3, 4, 5, 6) and a general trend has been established in nickel alloy 718. High temperature solution anneals (1500-2000F) accentuate IHC (4, 5, 6), low temperature solution anneals (1700-1750F) reduce IHC (3, 4, 5, 6), and age hardening (1400-1200F) accentuates IHC (3, 5, 6). The effect of heat treatment on IHC has been attributed to both intergranular precipitation reactions (4, 7, 11) and intergranular segregation (6, 12). Grain growth during heat treatment and pinning by matrix precipitates have also been offered as partial explanation (unpublished research by Thompson, Mayo, and Radhakrishnan).

The present study undertakes to identify the relative importance of intergranular segregation and precipitation in IHC. It also attempts to identify during which heat treatments segregation and precipitation are active at the grain boundaries and how this activity correlates with IHC susceptibility.

EXPERIMENTAL PROCEDURE AND RESULTS

A cast nickel alloy 718 (Table 2) was used in this study. It was modified to have two different carbon levels (0.02 and 0.06) and each carbon level had three sulfur levels (0.0008, 0.005, 0.009) for a total of six compositions. The alloys were cast into 6" x 1" x 1/4" test specimens.

TABLE 2

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Nb</th>
<th>Mo</th>
<th>Ti + Al</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>53.77</td>
<td>20.46</td>
<td>16.55</td>
<td>4.39</td>
<td>3.15</td>
<td>1.62</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Figure 1 The IHC susceptibility as a function of sulfur content for two different bulk carbon levels. Note that the effect of sulfur appears independent of the carbon level.
The IHC susceptibility of these alloys in the as cast and heat treated conditions was tested in a spot welding fixture called the spot varestraint test. The total length of cracking in a test was taken as the measure of a specimen's susceptibility to IHC. Figure 1 shows the effect of bulk sulfur on the IHC of alloy 718 in the as cast condition. Note that it is independent of carbon content and that IHC increases with bulk sulfur concentration. Figure 2 shows the effect of a 2000F heat treatment on IHC susceptibility. Note that the increase in cracking due to the heat treatment is independent of the bulk sulfur concentration. Figure 3 gives more results on IHC as a function of heat treatment. Using the as cast condition as a reference, note that 2000F and 1200F treatments for one hour increase IHC. The 1700F treatment for one hour has an opposite effect and these results are consistent with other studies on both cast and wrought alloy 718 (2, 3, 4, 5, 6).

Figure 2  
IHC susceptibility as a function of bulk sulfur concentration for the 0.06C alloy. Note that heat treatment effect appear independent of sulfur concentration.

Figure 3  
IHC susceptibility as a function of heat treatment for the 0.009S alloy.
Segregation at 2000F

<table>
<thead>
<tr>
<th>T°C</th>
<th>S</th>
<th>Nb</th>
<th>Ti</th>
<th>C</th>
<th>Δ t(Hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.T.</td>
<td>0.064</td>
<td>0.032</td>
<td>0.288</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1099</td>
<td>1.47</td>
<td>0.352</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1087</td>
<td>1.41</td>
<td>0.294</td>
<td>0</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>1080</td>
<td>1.55</td>
<td>0.263</td>
<td>0</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>1081</td>
<td>1.57</td>
<td>0.263</td>
<td>0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>922</td>
<td>1.86</td>
<td>0.369</td>
<td>0</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>923</td>
<td>1.78</td>
<td>0.339</td>
<td>0</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>670</td>
<td>1.95</td>
<td>0.375</td>
<td>0</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>953</td>
<td>2.19</td>
<td>NM</td>
<td>0</td>
<td>4.91</td>
<td></td>
</tr>
</tbody>
</table>

Segregation at 1200F

<table>
<thead>
<tr>
<th>T°C</th>
<th>S</th>
<th>Nb</th>
<th>Ti</th>
<th>C</th>
<th>Δ t(Hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.T.</td>
<td>0.104</td>
<td>0.059</td>
<td>0.298</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>651</td>
<td>0.32</td>
<td>0.35</td>
<td>0.8</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>645</td>
<td>0.4</td>
<td>0.32</td>
<td>0.65</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>645</td>
<td>0.414</td>
<td>0.365</td>
<td>0.68</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>657</td>
<td>0.52</td>
<td>0.4</td>
<td>0.72</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>661</td>
<td>0.48</td>
<td>0.385</td>
<td>0.70</td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td>661</td>
<td>0.41</td>
<td>0.3</td>
<td>0.6</td>
<td>8.33</td>
<td></td>
</tr>
<tr>
<td>657</td>
<td>0.39</td>
<td>0.3</td>
<td>0.6</td>
<td>19.50</td>
<td></td>
</tr>
<tr>
<td>660</td>
<td>0.38</td>
<td>0.25</td>
<td>0.5</td>
<td>24.00</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4 Auger peak height data (ratio with Ni 848 ev) of segregation to alloy 718 free surface during 2000F heat treatment in Auger system at $1 \times 10^{-3}$ torr.

Figure 5 Auger peak height data (ratio with Ni 848 ev) of segregation to alloy 718 free surface during 1200F heat treatment in Auger system at $1 \times 10^{-3}$ torr.

Figures 4 and 5 show free surface segregation behavior during the 2000F treatment (and includes information on slow cool down) and 1200F treatment. This data was collected by sputter cleaning a surface under vacuum in the Auger spectrometer and using an in situ hot stage to heat treat the sample during data collection. The 2000F treatment obviously releases sulfur for segregation to interfaces. This is not true of the 1200F treatment. However, some Nb and C segregation is indicated at 1200F.

Figures 6 and 7 show how heat treatment produces a strong grain boundary etch. The grain boundaries after a 1700F treatment show a strong Ni$_3$Nb(S) phase precipitation and TEM work is currently underway to identify other grain boundary precipitates.

Figure 6 As cast microstructure after oxalic acid etch. Note that grain boundary etch is light, if visible at all. 200X

Figure 7 Microstructure after treatment at 2000F for one hour plus 1700F for one hour and etched in oxalic acid. Note strong etching of grain boundaries. 200X
Figure G Changes in secondary phases during neat treatment. A. as cast  B. one 
hour at 2000F plus one hour at 1700F  C. one hour at 2000F plus one 
hour at 1200F.  all at 500X

Figure 8 shows that along with grain boundary segregation and precipitation 
during heat treatment, there is a general trend of phase change. The most notable 
changes occur at 2000F where the Laves phase dissolves (or after which this phase 
is no longer attacked by oxalic or Kalling's etchants) and at 1700F where a strong 
$\text{Ni}_2\text{Nb}$ precipitation occurs.

It has been shown in previous studies that liquation of $\text{NbC}$ (3, 5) and/or 
Laves phase (4, 16) is a prerequisite in the mechanism of IHC in alloy 718. The 
effect of heat treatment on controlling the distribution of these phases appears 
to correlate with IHC susceptibility. Figure 9 shows a general trend for all 
treatments which is a decreasing volume fraction of liquid with decreasing 
temperature after liquation. Perhaps more importantly, it also shows a decreasing 
connectivity of intergranular liquid. This observation is substantiated with 
volume fraction measurements of the liquid phase given in Figure 10. Figure 11 
shows the mechanism by which heat treatment affects IHC susceptibility. It shows 
that the intergranular liquid phase distribution (ILPD) on cooling is affected by 
heat treatment. A heat treatment involving 1200F causes the liquid to wet the 
grain boundary to lower temperatures during cooling than metal treated at 1700F. 
This correlates with IHC susceptibility which shows that 1200F treatments increase 
IHC while 1700F treatments decrease IHC.

Figure 9 Intergranular liquid phase distribution (ILPD) as a function of cooling 
temperature. All samples were heated to 2160F and quenched during cool 
down at the indicated temperature. Heat treated for one hour at 2000F 
plus one hour at 1200F. 500X
Fig. 10 A quantitative microstructural analysis substantiates that the volume fraction of liquid decreases more rapidly with cooling temperatures when a 1700°F heat treatment is used prior to liquation.

DISCUSSION

The role of intergranular chemistry on IHC has been difficult to identify. The main reasons for this were:

- alloy heats with the highest bulk impurity concentration did not always have the highest intergranular impurity concentrations,
- volume fraction of detrimental phases such as carbide, laves, and boride do not necessarily correlate with the intergranular volume fraction of these phases,
- the dependent and independent roles of intergranular solute segregation and intergranular precipitation were not understood relative to processing and heat treatment,
- the relative effects of intergranular segregation and precipitation on the magnitude of IHC were not understood.

Figure 11 suggests that heat treatments which cause intergranular liquid wetting at low temperatures also increase IHC. This suggests that the only portion of the alloy chemistry which affects IHC are those elements and phases in the grain boundary region at the time of welding. That is why process history prior to welding will have as strong, or stronger, an effect on IHC than alloy chemistry.

Bulk Solute Concentration Versus Intergranular Solute Segregation

Figure 1 shows that a bulk solute like sulfur will increase IHC. The as cast condition has interdendritic grain boundaries and the intergranular sulfur concentration ($X_S^I$) apparently follows a standard segregation isotherm where

$$\frac{X_S^I}{X_S^B} \propto \frac{X_S^B}{X_S^B}$$

An increasing intergranular sulfur concentration with increasing bulk sulfur would give an increase in IHC. Figure 2, when taken with Figure 4, is interesting because it suggests that the effect of high temperature annealing (2000°F) is related to the release of sulfur. It also shows that at 2000°F, equation 1 is probably obeyed again. Based on the relative differences in IHC ($\Delta$IHC) (see
example 3) between sulfur released at 2000F (ΔIHC \(_{2000F}\)) and the sulfur range studied (ΔIHC \(_{\overline{X}_5}\)), it is seen that

\begin{align}
\Delta \text{IHC}_{2000F} & \leq \Delta \text{IHC}_{\overline{X}_5} \\
1.9 \text{ mm} & < 3.6 \text{ mm}
\end{align}

This means that prior processing can mask attempts to correlate IHC with bulk impurity levels due to the sulfur distribution. It also means that heat-to-heat chemistry can mask attempts to correlate IHC with annealing temperature.

**Dependent and Independent Roles of Intergranular Solute**

Figures 3, 4, and 5 give a new understanding to the relationships between heat treatment, intergranular solute, and IHC. Individually, treatments of one hour at 2000 and one hour at 1200 both increase IHC. Figure 4 suggests that the effect of the 2000F treatment is related to sulfur segregation; however, Figure 5 shows that sulfur segregation does not occur at 1200F. There must be a contribution to IHC at 1200F which is independent of sulfur and which possibly is related to the observed Nb and C segregation. Volume fraction measurements show that both NbC and Laves phase are dissolved during the 1200F heat treatment. The observed Nb and C segregation could be associated with the redistribution of these matrix phases to the grain boundary. If the segregation is a precursor to NbC intergranular films, then a strong mechanism is established for increased IHC independent of the sulfur effect.

The possibility that these two effects are not only independent but additive can be shown with example 3. Examine the increase in IHC associated with these heat treatments:

![Temperature dependence of ILPD as a function of heat treatment. All samples were heated to 2160°F and quenched during cool down at: A. quenched at 2160°F, heat treated as indicated. B. quenched at 2040°F, heat treated as indicated.](image-url)
By looking at the change relative to the as cast reference it can be shown that

4) \( (1 \text{ hr. } @ 2000\text{F}) + (1 \text{ hr. } @ 1200\text{F}) \approx (1 \text{ hr. } @ 2000\text{F} \text{ plus } 1 \text{ hr. } @ 1200\text{F}) \)
\[ \Delta \text{IHC}_{2000} + \Delta \text{IHC}_{1200} \approx \Delta \text{IHC}_{(2000 + 1200)} \]
\[ 1.9 \text{ mm } + 4.6 \text{ mm } \approx 6.1 \text{ mm} \]

Applying the same logic to the 1700F heat treatment:

5) \( (1 \text{ hr. } @ 2000\text{F}) + (1 \text{ hr. } @ 1700\text{F}) \approx (1 \text{ hrs. } @ 2000\text{F} \text{ plus } 1 \text{ hr. } @ 1700\text{F}) \)
\[ \Delta \text{IHC}_{2000} + \Delta \text{IHC}_{1700} \approx \Delta \text{IHC}_{(2000 + 1700)} \]
\[ 1.9 \text{ mm } + 4.23 \text{ mm } \approx -0.24 \text{ mm} \]

The answers for the 1700F treatment does not match as fortuitously as did example 4 but the answer is in the right direction, i.e., a net reduction. The magnitude of \( \Delta \text{IHC}_{1700} \) is similar, but of the opposite sign, to \( \Delta \text{IHC}_{1200} \) indicating that it may be a precipitation reaction instead of a solute segregation reaction. Metallography also indicated a strong \( \text{Ni}_3\text{Nb} \) precipitation near the grain boundaries during the 1700F treatment (Figure 7).

Relative Magnitudes of IHC Related to Precipitation and Segregation

Examples 2, and 5, involving \( \Delta \text{IHC} \), make it clear that the bulk sulfur level has a limited effect on IHC as compared to heat treatment which exerts more control over intergranular chemistry. There appears to be a well defined difference also between the magnitude \( \Delta \text{IHC} \) resulting from sulfur segregation during heat treatment and possible precipitation reactions.

NEEDED RESEARCH

1. Free surface segregation data is needed at 1700F.
2. The critical temperature at which sulfur is released to the free surface is needed.
3. Free surface segregation at a second bulk sulfur level is needed at 2000F to determine if that heat treatment obeys \( X_\alpha \times X_\beta \) as suggested by IHC data.
4. Transmission electron microscope identification of the grain boundary precipitate structure is needed for all heat treatments.

CONCLUSIONS

The primary metallurgical contribution to the mechanism of intergranular hot cracking during welding is intergranular chemistry. Intergranular chemistry influences the temperature dependence of the intergranular liquid distribution and thereby helps dictate if a liquid film is present when residual welding stress develops.
Contributions to the intergranular chemistry come from: the concentration of solute (in this case S) in solution, the release of solute from precipitates during heat treatment (in this case S, Nb and C), and segregation of solute to grain boundaries leading to monolayer coverage and precipitation. Auger spectroscopy results support the conclusion that sulfur forms monolayer coverages during primary processing and again during high temperature solution annealing (2000F). Significant Nb and C segregation occur at 1200F and it is postulated that this leads to NbC intergranular film which is the cause of the large increase in intergranular hot cracking susceptibility after this treatment. More work is needed to reach conclusions concerning the mechanism associated with improved crack resistance following the 1700F treatment.

The changes in intergranular hot cracking (Δ IHC) associated with the 2000F treatment and 1200F treatment suggest these mechanisms are independent and of different magnitudes. This supports a combined monolayer S segregation and NbC precipitation explanation of a multiple 2000F + 1200F heat treatment.

The relative magnitudes of IHC associated with various contributions to the intergranular chemistry are within a factor of three. Individually this difference would seem small except that it has been shown that at least three contributions are additive. This means that a relative contribution to IHC from a series of negative contributions (i.e., high sulfur, 2000F plus 1200F treatment) could overwhelm a contribution from a single positive source. This also explains why it is so difficult to correlate variables with IHC when using data from various heats and different process histories.

Acknowledgements

The authors wish to thank Dr. C. L. Briant of G.E. Corporate Research and Development for supplying the hot stage Auger spectroscopy analysis. They are also grateful to the National Science Foundation for supporting this work under grant DMR-8503216 and the G.E. Gas Turbine Division for supplying samples.

References