Original Article

Oxidation assisted intergranular cracking in 718 Nickel Superalloy: on the mechanism of dynamic embrittlement

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Abstract

Nickel Superalloy 718 was specially designed for high temperatures. However, due to an embrittlement phenomenon, its application is limited up to 650 °C. This work presents a contribution to the understanding of the embrittlement mechanism focusing on the crack propagation kinetics responsible for the brittle fracture. This manifestation is known as OAIC (Oxidation Assisted Intergranular Cracking), although the phenomenology resulting in such degradation is not well understood. The approach to the problem was accomplished in the solubilized condition by mechanical testing, fractography and activation energy calculation. Generally, high temperature dissociation of NbC in the presence of oxygen is pointed as the source of niobium that ultimately lead to fracture by Nb2O5 formation at grain boundaries. However, metallographic analysis of fractured samples between 600 and 925 °C at different strain rates indicated otherwise. Samples tested at 850 °C showed minimum ductility and fast intergranular crack propagation, at a short time incompatible with carbide dissociation and Nb2O5 formation. Furthermore, there is no evidence of sufficient NbC along grain boundaries to supply elemental niobium to the formation of the Nb2O5 continuous film. Besides, onset to OAIC as a function of temperature and strain rate led to a 223 kJ/mol activation energy, which can be associated to niobium self diffusion within the matrix. Considering that the dynamic aging phenomenon and the γ′ precipitation occur concomitantly with the deformation, the results suggest that niobium segregation together with preferential γ′ precipitation at grain boundary and the consequent stress state build up should play also a decisive role in the embrittlement.

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1. Introduction

Nickel based superalloys are a good benefit-cost ratio material for challenging environments, such as high temperatures, pressures as well as oxidizing atmospheres. This remarkable performance is mostly due to great mechanical properties, oxidation resistance and high-temperature structural stability. Particularly, INCONEL® 718 (IN-718) has a great commercial value and has been used for decades in nuclear and aerospace industries, representing the highest manufactured type among them [1]. Its Ni–Fe–Cr matrix is precipitation hardened by the γ’ (Ni3Al,Ti) and γ” (Ni3Nb) phases. Additionally, the expressive amount of niobium in this alloy favors its segregation throughout grain boundaries, MC carbide formation and γ” precipitation, playing an overall important role in the microstructure [2]. Since IN-718 industrial applications, as in turbine jet engines, nuclear reactors and power plants, are intimately correlated to the alloy’s microstructural integrity, understanding any atypical behavior is crucial to guarantee its safe operation.

It is reported that while IN-718 under load is exposed between 650 °C and 850 °C approximately, the phenomenon referred as OAIC occurs and embritts the alloy [3,4]. As a result, an undesired change in the fracture mode is observed at these temperatures, weakening IN-718 mechanical properties. Pang et al. [5] identified 20 years ago a probable association between intergranular fracture of polycrystalline IN-718 samples exposed to 700 °C and the surface enrichment of niobium in creep crack growth experiments. However, most subsequent studies have suggested niobium carbide (NbC) dissociation in the presence of oxygen as the main niobium source for inducing brittle oxide formation of Nb2O5 at the grain boundaries [6-8]. Addition of combined temperature and tension would ultimately result in grain boundaries decohesion. Thereafter, several authors have propagated this assumption, supported by evidence of feathery-like NbC after long hours of high temperature exposure, even though the Nb2O5 characterization is hardly found in the literature [9]. Oxygen by itself is also considered an alternative controlling variable [10,11]. Huang et al. [10] performed sustained-load crack growth experiments in a Nb-containing alloy and a Nb-free alloy to prove brittle cracking was a result of stress-enhanced diffusion of oxygen into the crack-tip. Results showed that crack growth rates in oxygen atmosphere were faster as the temperature increased for both alloys, suggesting relative independence of the niobium content. Despite the numerous studies on this topic, there is no consistent explanation regarding the mechanisms involved or their dependency on thermodynamic variables.

Thereby, the objective of the present study was presenting an approach that considers the kinetics of the intergranular crack growth at temperatures corresponding the minimum of ductility.

2. Methods

The chemical composition of the IN-718 used in this study is described in Table 1. The material was provided by Villares Metals S.A. in the form of a forged bar with a diameter of 170 mm and length of 800 mm. The nickel superalloy was melted in a vacuum induction furnace, re-melted in a vacuum arc furnace, homogenized via heat treatment, and hot-forged through an open-die forging process in a 2000 ton press. Cylindrical tensile specimens were machined from the rolled direction of the bar and then submitted to a vacuum solution annealing treatment at 1050 °C during 1 h, followed by water cooling. Hot tensile tests were then performed under secondary vacuum of 1.7 x 10^-2 mbar at strain rates of 3.2 x 10^-3 s^-1, 3.2 x 10^-4 s^-1 and 3.2 x 10^-5 s^-1, in temperatures ranging from 600 to 925 °C. The furnace was pre-heated to the test temperature before the specimens were charged. Extra tensile test at 850 °C was performed and stopped before fracture at different strain levels. The microstructure of the fractured samples in the longitudinal section was then observed by scanning electron microscopy (SEM) and by transmission electron microscopy (TEM). To expand the details of this investigation, a composition mapping by Energy Dispersive Spectroscopy (EDS) was also performed. Sample preparation for SEM observations consisted of polishing and etching with hydrochloric, nitric acid, acetic acid and glycercin (15 mL HCl + 10 mL HNO3 + 10 mL CH3COOH + 5 mL C2H6O2). Samples for TEM examinations were produced from the Focused Ion Beam (FIB) technique. The activation energy for the OAIC start was calculated using the Arrhenius equation for three different onset temperatures at the three strain rates.

3. Results

3.1. Microstructure

The solution annealed Inconel 718 observed by SEM and TEM presented a γ-matrix with mostly equiaxial grains, a few primary carbides (Nb,Ti)C at the grain boundaries and several twin boundaries. The material in this condition was free of the hardening phases γ’ and γ” as well as delta phase. The described microstructure is shown in Fig. 1.

3.2. Hot tensile testing

Fig. 2 present the stress–strain curves for the temperatures of mechanical tests at 3.2 x 10^-4 s^-1. This strain rate will represent the details of this investigation. In order to better access the mechanical response, elongation and yield strength parameters were extracted in each case to create a graph of ductility and strength vs temperature (Fig. 3). The results show a region of minimum ductility associated to a peak of resistance in the intermediate temperatures of the analyzed range. Table 2 presents a list of yield strengths, elongation percentages and times for rupture for the temperature interval. The serrated flow, observed in the first temperatures, is characteristic of IN-718 and it will impact the mechanical properties as well. Precipitation of the hardening phases γ’ and γ” is also expected to occur dynamically and, therefore, to contribute to the listed values showing a peak of resistance in the intermediate temperatures.
Fig. 1 – Stress–strain curves for solution annealed IN-718 tested between 600 and 925 °C at 3.2 × 10⁻⁴ s⁻¹.

Fig. 2 – Mechanical properties of solution annealed IN-718 tested between 600 and 925 °C at 3.2 × 10⁻⁴ s⁻¹.

3.3. Fractography

The surface fractures from SEM are shown in Fig. 4. At 600 °C, the presence of dimples indicated clearly a ductile fracture. Yet, from 650 °C it is possible to identify intergranular brittle fracture at the samples edges. The brittle aspect is known to progress toward the interior of the sample until it takes over the surface completely [3], which is illustrated by the samples tested at 700 °C and 850 °C. The former temperature shows a mixed type of fracture in the center, while in the latter the fractured surface is completely intergranular. Because of this, 850 °C temperature was then considered the minimum ductility specimen. At 900 °C, the presence of cavities marks the return to the ductile behavior.

Fig. 5(a)–(c) shows longitudinal sections of suggested transition temperatures 650 and 900 °C, together with completely brittle fracture at 850 °C. The transition temperatures 650 and 900 °C revealed the occurrence of several secondary cracks along the section length in a relatively low magnification, while these features were not observed at the minimum ductility at 850 °C. However, a similar aspect showing the crack that would lead to fracture was found for the interrupted test sample at 94% of its total deformation (Fig. 5d). This means that the intergranular crack was formed two minutes before the fracture, considering the total time for rupture presented in Table 2.

Table 1 – Chemical composition of IN-718 (% weight).

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>52.3</td>
</tr>
<tr>
<td>Cr</td>
<td>18.4</td>
</tr>
<tr>
<td>Ti</td>
<td>1.02</td>
</tr>
<tr>
<td>Co</td>
<td>0.042</td>
</tr>
<tr>
<td>Mo</td>
<td>2.8</td>
</tr>
<tr>
<td>Cu</td>
<td>0.026</td>
</tr>
<tr>
<td>Nb</td>
<td>5.1</td>
</tr>
<tr>
<td>Mn</td>
<td>0.017</td>
</tr>
<tr>
<td>Al</td>
<td>0.57</td>
</tr>
<tr>
<td>Fe</td>
<td>18.2</td>
</tr>
<tr>
<td>C</td>
<td>0.04</td>
</tr>
<tr>
<td>P + S</td>
<td>&lt;0.005</td>
</tr>
</tbody>
</table>

Fig. 3 – Graph of ductility vs yield strength for the tensile tested specimens between 600 and 950 °C, showing a sharp decrease in ductility simultaneously with a peak of strength at intermediate temperatures.

Table 2 – Data results of yield strength, elongation and time for rupture from the mechanical testing between 600 and 925 °C at 3.2 × 10⁻⁴ s⁻¹.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Yield strength (MPa)</th>
<th>Elongation (%)</th>
<th>Time for rupture (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>236.43</td>
<td>71.39</td>
<td>37.41</td>
</tr>
<tr>
<td>625</td>
<td>231.28</td>
<td>71.12</td>
<td>38.47</td>
</tr>
<tr>
<td>650</td>
<td>229.09</td>
<td>73.35</td>
<td>37.62</td>
</tr>
<tr>
<td>670</td>
<td>207.88</td>
<td>64.97</td>
<td>34.26</td>
</tr>
<tr>
<td>700</td>
<td>320.77</td>
<td>41.56</td>
<td>30.52</td>
</tr>
<tr>
<td>850</td>
<td>448.95</td>
<td>20.38</td>
<td>11.84</td>
</tr>
<tr>
<td>900</td>
<td>202.49</td>
<td>40.81</td>
<td>21.59</td>
</tr>
<tr>
<td>925</td>
<td>148.39</td>
<td>99.95</td>
<td>53.92</td>
</tr>
</tbody>
</table>

EDS mapping near the edges of fracture of the samples at the minimum ductility temperature range presented a poorly defined interface between (Nb,Ti)C carbides and the matrix, besides dissolved niobium around them, as exemplified in Fig. 6 for 650 °C. In turn, TEM analysis confirmed an intensive precipitation of mostly γ’ and γ for 700 °C (Fig. 7) and δ phase at 900 °C (Fig. 8). These regions were also mapped by EDS, showing the high content of Al, Ti and Nb for the first case and Nb and Ti for the latest.

3.4. Activation energy

Table 3 presents the OAIC start temperatures \(T_{OAIC}\) at the respective deformation rates. The activation energy given by the Arrhenius equation was 223 kJ/mol. The result comprehends reported values for niobium self-diffusion in nickel matrix [12,13].

4. Discussion

Solution annealed IN-718 shows a loss of ductility between 650 °C and 850 °C. This occurrence known in the literature as OAIC was identified based on the criterion of intergranular fracture evidenced by SEM and significant decrease in ductility. At this temperature interval, dynamic strain aging and the dynamic precipitation of mostly γ’ occur simultaneously. Even though both phenomena may result in yield strength increase, the sharp fall in ductility is not justified by them. On the other hand, they explain the peak of resistance observed in the region of minimum ductility. It is also important to observe that at complete brittle failure observed by SEM at 850 °C only dynamic precipitation occurs. Considering the effects of precipitation, it is true that an intergranular precipitation could lead to the grain boundaries decohesion in particular conditions.
Fig. 5 – SEM (SE) images of the longitudinal sections of samples tested at $3.2 \times 10^{-4}$ s$^{-1}$ at the transition temperatures of 650 °C (a) and 900 °C (b), as well as the minimum ductility temperature 850 °C (c). The specimen surface of the interrupted tensile test at 850 °C is also presented (d). The transition temperatures show quite a few secondary cracks at low magnification, while at 850 °C they only appear in the last two minutes of the test.

Fig. 6 – EDS mapping by SEM of the fractured section at the transition temperature 650 °C (a) for Nb (b) and Ti (c) major elements. There is indication of niobium dissolution and a poorly defined interface between (Nb,Ti)C and the matrix.

Fig. 7 – TEM image (HAADF) of the 700 °C/3.2 $\times$ 10$^{-4}$ s$^{-1}$ specimen at a grain boundary region (a). Intensive precipitation is revealed by EDS mapping with $\gamma''$ and $\gamma'$ represented by the contents of Nb, Al (b) and Ti (c).
Fig. 8 – TEM image (HAADF) of the 900 °C/3.2 x 10^{-4} s^{-1} specimen at a grain boundary region (a). Intensive precipitation is revealed by EDS mapping with δ represented by the contents of Nb (b) and Ti (c).

Table 3 – Temperature and strain rate dependence used in activation energy calculations for the onset of the minimum ductility temperature range.

<table>
<thead>
<tr>
<th>T_{OAC} (°C)</th>
<th>T_{OAC} (K)</th>
<th>Strain rate (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>1023</td>
<td>0.001</td>
</tr>
<tr>
<td>650</td>
<td>923</td>
<td>0.0001</td>
</tr>
<tr>
<td>600</td>
<td>873</td>
<td>0.00001</td>
</tr>
</tbody>
</table>

[14]. Additionally, Rezende [3] found a reduced temperature interval for the minimum in ductility in aged samples. These data support direct influence of the dynamic precipitation on the studied mechanism. Also, consistent with the TTT diagram for alloy 718, the literature reports precipitation beginning at around 600 °C, while 850 °C coincides with nearly instantaneous clustering of particles and, therefore, the maximum kinetics of precipitation [15]. When addressing the occurrence of multiple secondary cracks 120°s before the rupture, it points to a very fast nucleation and propagation of these cracks, which is incompatible with the long aging times in which NbC dissociation has been reported [9,16]. Throughout this investigation, the relative small amount of NbC at the grain boundaries questions whether they could provide enough of the niobium element to form a brittle oxide in the presence of oxygen. Also, the NbC oxidation should be rapid enough to occur within a few seconds of tensile test. The presence of Nb_{2}O_{5} on the fracture surface or associated with the secondary cracks could not be confirmed.

The value of a 223 kJ/mol activation energy for the phenomenon manifestation reveals niobium diffusion as the controller mechanism to the embrittlement. It also corroborates the hypothesis of precipitation as the dominant factor, since niobium segregates to the grain boundaries to form Ni_{3}Nb in short periods of time [15].

5. Conclusion

The present results suggest that the main mechanism for the minimum in ductility observed to the solution annealed IN-718, known in the scientific literature as OAIC, involves primarily the segregation of Nb to grain boundary and a strain-induced fine precipitation of γ′, ultimately resulting in a change of fracture from ductile transgranular to brittle intergranular mode. Activation energy calculation of 223 kJ/mol shows niobium self-diffusion in nickel matrix as the controller mechanism for the phenomenon. Strain-induced fine precipitation of γ′ explains the peak of resistance in the minimum ductility temperature range.

Considering also that metallographic observation shows a relative small amount of NbC at the grain boundaries and that the presence of Nb_{2}O_{5} on the fracture surface or its association with the secondary cracks could not be confirmed by SEM or TEM, the most used explanation to the phenomenon cannot be consistently be applied to explain its occurrence under conditions considered in the present paper.

Conflicts of interest

The authors declare no conflicts of interest.

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