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Environmentally-assisted grain boundary attack as a mechanism of embrittlement in a nickel-based superalloy

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The loss of ductility in the high strength polycrystalline superalloy 720Li is studied in air between room temperature and 1000 °C. Tensile ductility is influenced profoundly by the environment, leading to a pronounced minimum at 750 °C. A relationship between tensile ductility and oxidation kinetics is identified. The physical factors responsible for the ductility dip are established using energy-dispersive X-ray spectroscopy, nanoscale secondary ion mass spectrometry and the analysis of electron backscatter diffraction patterns. Embrittlement results from internal intergranular oxidation along the γ-grain boundaries, and in particular, at incoherent interfaces of the primary γ' precipitates with the matrix phase. These fail under local microstresses arising from the accumulation of dislocations during slip-assisted grain boundary sliding. Above 850 °C, ductility is restored because the accumulation of dislocations at grain boundaries is no longer prevalent.

1. Introduction

Polycrystalline γ/γ'-strengthened Ni-based superalloys are very strong, but their grain boundaries are a source of weakness at elevated temperature due to their interaction with gaseous environments containing oxygen. This problem is of particular concern when considering the application of these materials in the hot-section components needed for power generation and/or jet propulsion: these are subjected to oxidative and corrosive gas streams whilst under high stresses at temperatures in excess of 700 °C. Operating temperatures are rising markedly – due to ongoing fuel efficiency demands and the need to reduce emissions – hence damage from so-called environmentally-assisted cracking is becoming increasing prevalent and is now the major limitation to the application of Ni-based superalloys at the higher temperatures [1]. The precise mechanism for this effect is contentious, necessitating systematic experimentation and associated characterisation at the appropriate length scale to elucidate the underlying physical and chemical factors at play.

Environmentally-assisted cracking has been proposed by some investigators to be influenced by dynamic embrittlement involving the migration of elemental oxygen ahead of the crack front [2–5]; others propose that the phenomena is affected by stress-assisted grain boundary oxidation (SAGBO) [6–9]. The distribution of oxygen at an intergranular crack tip has been characterised recently using techniques of high spatial resolution including transmission electron microscopy combined with energy dispersive X-ray spectroscopy (EDX) [9], nanoscale secondary ion mass spectrometry (NanoSIMS) [10], and atom probe tomography [8]. These studies revealed the formation of a layered oxide structure along the γ-grain boundaries ahead of the cracks thus supporting a damage mechanism similar to the SAGBO concept. In general, the layering was found to be in agreement with thermodynamics: thermodynamically unstable oxides consisting of Ni, Fe and Co were found at the beginning and centre of the crack while more stable oxides consisting of Cr, Ti and Al were found closer to the interface of the oxide and metal [6,8,11]. The oxidation of secondary γ'-precipitates has been suggested to lead to the formation of Ni- and Al-rich oxides [8]. However, the proposed concepts so far fail to explain fully why a super-solvus heat treatment with only intragranular γ'-precipitates is observed to be more resistant to environmentally assisted cracking than a sub-solvus heat treatment where both intra- and intergranular γ'-precipitates are present [12].

In the literature, environmentally-assisted cracking is most usually recognised in the context of low-cycle fatigue and dwell-fatigue loading tests. However, the complexity of such testing

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combined with the substantial time and material requirements is somewhat problematic. Alternatively, Gabb et al. [13] demonstrated that inelastic failure strain of slow strain-rate tensile tests can be correlated to the dwell fatigue crack propagation rate. Here, these pioneering concepts are built upon. Sub-solvus heat treated superalloy 720Li is subjected to slow strain-rate tensile tests between room temperature and 1000 °C. Miniature test pieces of enhanced surface/volume ratio are employed, in order to accelerate the embrittlement effect and thus facilitate its study. These miniaturised tensile tests have been shown to be capable of capturing the temperature and time-dependent effects that occur during environmentally-assisted failure [14]. In the past, a temperature dependent minimum in tensile ductility [15,16] and maximum in fatigue crack propagation rate [17] was observed. This was reviewed by Woodford [18] who proposed that a mid-temperature embrittlement is not exclusively due to environmental interactions but is also linked to the grain boundary mobility. This hypothesis is not incompatible with more recent results which emphasise that the ability to reduce stresses at the crack tip by stress relaxation has an impact on an alloy's susceptibility to oxidation-assisted cracking [9,19,20].

In this study, quantitative data for the ductility of alloy 720Li are reported and the role of environmental attack is confirmed. Detailed characterisation of the crack tip processes is then carried out – notably with EDX, NanoSIMS and high resolution electron backscatter scatter diffraction (HR-EBSD) in an attempt to answer the following questions:

(1) What is the nature of the environmentally-assisted grain boundary attack leading to intergranular crack propagation?
(2) What is role of the deformation mechanism on the failure of the environmentally-induced damage zone?
(3) How can we rationalise the effect of heat treatment on an alloy's susceptibility to environmentally-assisted cracking?

2. Experimental procedure

2.1. Material

In this study, the cast/wrought nickel-based superalloy alloy 720Li was used primarily. A further more limited number of tests were carried out on the powder metallurgy alloy RR1000. Nominal compositions are given in Table 1. The materials were supplied by Rolls-Royce plc. in the form of fully heat treated forgings.

Alloy 720Li has a temperature capability of around 700 °C [21]. The following sub-solvus heat treatment was applied: a solution heat treatment at 1095 °C for 4 h followed by an oil quench and a subsequent ageing heat treatment at 760 °C for 16 h. Fig. 1(a) shows the as-received microstructure of alloy 720Li prior to testing. This region was investigated using EBSD in order to calculate the γ-grain and primary incoherent γ'-precipitate size distribution, see Fig. 1(b). A Gaussian non-linear curve fit was applied in order to distinguish the average γ-grain size, $d_\gamma \approx 8 \pm 3$ μm, and the average intergranular primary γ'-precipitate size, $d_{\gamma'} \approx 4 \pm 0.5$ μm. The size of these intergranular primary γ'-precipitates can be determined using EBSD because their incoherency results in a crystal orientation which differs from the adjoining γ-grains. The measured average γ-grain and primary γ'-precipitate size is in close agreement with previous microstructural assessment of Alloy 720Li [22–25]. The mean diameter of the intergranular secondary γ'-precipitates which are shown in Fig. 1(c) was found to be $\approx$ 100 nm. For comparison, a super-solvus heat treatment at 1170 °C was applied to alloy 720Li. Unfortunately, due to the lack of grain boundary pinning after the dissolution of the primary γ'-precipitates abnormal grain growth occurred; the reason can be traced to the low content of grain boundary elements (Table 1). In addition, upon cooling at requisite rates, quench cracking was observed. As a result, alloy RR1000 processed by powder metallurgy was studied additionally in both sub- and super-solvus heat treated condition. The sub-solvus heat treatment consisted of a solution heat treatment at 1120 °C for 4 h followed by an air quench and an ageing heat treatment at 760 °C for 16 h which is reported to result in a γ-grain size of $d_\gamma \approx 7 \pm 2$ μm and a primary γ'-precipitate size of $d_{\gamma'} \approx 5$ μm [26]. The super-solvus heat treatment consisted of a solution heat treatment at 1170 °C for 1 h followed by an fan air cool and an ageing heat treatment at 760 °C for 16 h. This super-solvus heat treatment was shown to increase the γ-grain size to $d_\gamma \approx 30 \pm 5$ μm [26]. A full characterisation of the as-received microstructure of RR1000 can be found elsewhere [9,26–28].

Table 1
Nominal composition of alloy 720Li and RR1000 in wt-% (Ni-base).

Alloy	Ni	Cr	Co	W	Mo	Al	Ti	Ta	C	B	Zr
720Li	bal	16.0	15.0	1.25	3.0	2.5	5.0	0.0	0.015	0.015	0.035
RR1000	bal	15.0	18.5	0.0	5.0	3.0	3.6	2.0	0.027	0.015	0.06

2.2. Assessment of the tensile ductility

Tensile testing was conducted between room-temperature and 1000 °C on a 5 kN Instron electro-thermal mechanical testing (ETMT) machine [29]. Miniaturised specimens of cross-section 1 × 1 mm^2 and a gauge length of 14 mm were used; the full sample length was 40 mm. The specimens were produced using wire-based electrical discharge machining (EDM), with surfaces subsequently ground to 1200 grit finish using silicon carbide grinding paper to maintain a consistent surface finish and to remove the recast layer resulting from the EDM process. Temperature measurement during testing was achieved by spot-welding a K-type thermocouple to the central portion of the specimen gauge. A minimum of three tests were performed at each condition.

Slow strain-rate tests were performed in laboratory air with an initial slow strain-rate close to $1 \cdot 10^{-4}$ s^{-1}. These were conducted at room temperature, 400, 500, 600 and between 700 and 1000 °C in steps of 50 °C. Consistent with the design of the ETMT machine, specimens were heated using electrical resistance by passing a direct current through the specimen. Tests were performed at a constant extension rate using a linear variable displacement transformer (LVDT). The engineering strain was used as a measure of the ductility; engineering strain is defined as $\varepsilon = [(L_f - L_0)/L_0]$, where the gauge length extension $L_0 - L_f$ was monitored using digital image correlation following a thermal paint pattern in the central 5 mm of the specimen where the temperature and therefore deformation is uniform [14]; the engineering stress-strain curves produced were shown to be independent to small changes of L° (5 mm). Further but more limited testing was carried out at 800 °C using intermediate and fast initial strain-rates - close to $1 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ s^{-1} – in laboratory air. Slow strain-rate tensile testing was also conducted in argon at 800 °C.

2.3. Measurement of the oxide kinetics

Thermo-gravimetric analysis (TGA) was conducted on 10 × 10 × 1 mm test pieces between 700 and 1000 °C using a Netsch Jupiter TGA rig. Prior to isothermal exposure, specimen surfaces were ground to a 1200 grit finish using silicon carbide grinding paper. In addition, all edges were chamfered. Specimens were exposed between 700 and 1000 °C in 100 °C steps to 50 ml/min laboratory air for a short exposure time of 10 min and for a