Review

Gas phase embrittlement and time dependent cracking of nickel based superalloys

D. A. Woodford

Nickel based superalloys are critical to the safe operation of many energy conversion systems operating at high temperatures. Time dependent intergranular cracking of these alloys, under both sustained and cyclic loads, is dominated by environmental interactions at the crack tip. This review is concerned mainly with the interaction of oxygen in alloys used for combustion turbine discs, although interactions with other more aggressive species are considered. The phenomenology of this cracking is shown to be consistent with the same mechanism as that associated with oxygen embrittlement resulting from pre-exposure of uncracked material, and also with environmentally induced reduction in creep rupture life. Gas phase embrittlement (GPE), resulting from intergranular oxygen penetration, is shown to be responsible for all four streams of experimental observations. Three distinct processes of intergranular embrittlement involving oxidation reactions have been confirmed experimentally. One of these, the oxidation of intergranular sulphides, results in elemental sulphur embrittlement and subsequent local decohesion under stress. The other two, oxidation of carbon or carbides to form carbon dioxide gas bubbles and oxidation of strong oxide formers to form intergranular internal oxides, result in a reduction of the local ability to accommodate stress concentrations associated with sliding grain boundaries in an intermediate temperature range. This in turn leads to a temperature dependent minimum in ductility and maximum in crack propagation rate. Attempts to reduce the sensitivity to time dependent cracking based on chemistry (chromium level or trace element addition), microstructure control (using thermal–mechanical treatment or controlled cooling), or reversal of environmental embrittlement, are all considered. The conclusions form a basis for the development of life prediction methods for energy materials operating in diverse environments.

Keywords: Superalloys, High temperature alloys, Fatigue cracking, Creep rupture, Gas phase embrittlement, Oxidation, Intergranular fracture, Creep cavitation, Ductility minima

Introduction

Nickel based and Ni–Fe based superalloys used for discs or rotors provide a safety critical subsystem for gas turbines. Alloy IN718 has been the most extensively used of all superalloys for aircraft engine discs. As such there is an enormous amount of data on processing and properties. A similar alloy, IN706, containing less Ni, Nb, Al and Cr but more Fe and Ti and no Mo has been used for about 15 years in industrial gas turbines. The compositions of some of the more common wrought nickel alloys used in the gas turbine industry and discussed in the present report are listed in Table 1.

Superalloys are sensitive to environmental enhanced intergranular cracking in which the damaging species may be oxygen, or other more aggressive species such as water vapour, sulphur or chlorine. Special emphasis is placed in the present paper on current understanding of the phenomenology and mechanisms of damage associated with exposure to gaseous species. The author will in general avoid descriptive terms that imply specific mechanisms. However, gas phase embrittlement (GPE) appears to be sufficiently flexible to incorporate possible damaging species other than oxygen and oxidation. It can, moreover, relate to both bulk damage and crack tip damage.

Over the last half century investigation of GPE in nickel based and other engineering alloys has followed four main streams of investigation: cyclic stress or strain cracking (fatigue crack initiation and propagation), sustained load crack propagation (often misnamed creep crack growth), environmental embrittlement (effect of pre-exposure at high temperatures on subsequent intergranular fracture at lower temperatures), and creep fracture of smooth or notched specimens (nucleation and growth of creep cavities). Brief descriptions of the relevant aspects of studies in each experimental stream

Materials Performance analysis, Inc., 1707 Garden Street, Santa Barbara, CA 93101, USA

Corresponding author, email woodfordd@aol.com

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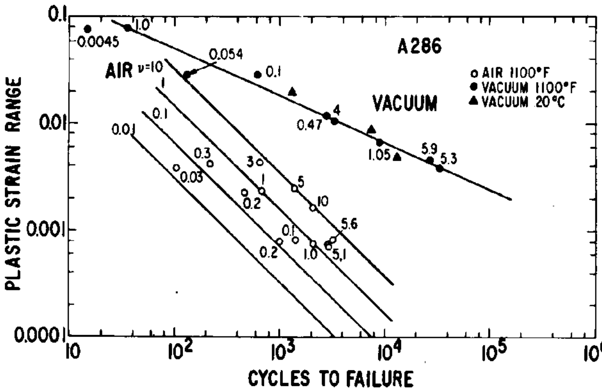
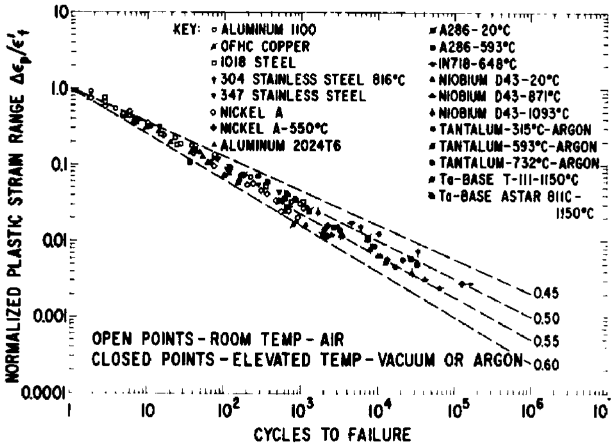


1 Plastic strain range *v.* fatigue life for A286 in air and vacuum at 593°C: numbers adjacent to test points indicate frequency, cpm (Ref. 5)



2 Plastic strain range *v.* cycles to failure for several metals in room temperature air and high temperature vacuum or argon: plastic strain range normalised to fatigue ductility[5]

will be given and the many proposed mechanisms summarised. Emphasis will be placed on the extensive literature on the effect of an oxygen containing environment. However, where pertinent, the effect of other species that could be present in some circumstances will be discussed. In particular, the compressed air environment for the disc could contain varying amounts of moisture, sulphur (in industrial environments) and chlorine (in oceanside environments).

High temperature time dependent cracking

Cyclic loading (fatigue)

Wrought nickel based superalloys are used in the gas turbine for high temperature high stress situations where fatigue damage[1] often limits their safe life. These alloys are strengthened by fcc gamma prime or metastable bct gamma double prime. They also may contain carbides and various impurities and compounds of impurities, notably sulphides.

It is usual and appropriate to consider fatigue strength to be dependent on two separable processes, namely crack initiation and crack propagation. However, many significant early studies of elevated temperature fatigue in superalloys used low cycle fatigue tests of smooth or notched specimens to evaluate the effects of test parameters on total fatigue life. These will be considered first.

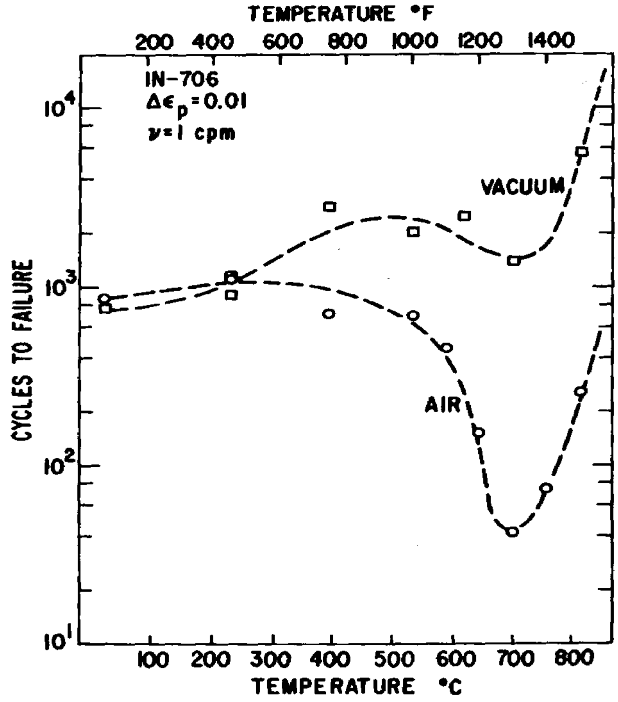
Low cycle fatigue

A number of studies in the early sixties on lead and indium,[2] copper and aluminium,[3] nickel and stainless steel[4] showed that low cycle fatigue (LCF) life at elevated temperatures increased as the oxygen partial pressure decreased. In some cases there appeared to be a sharp transition in life at a critical temperature sensitive partial pressure. This theme of environmental sensitivity at elevated temperatures was taken up by Coffin *et al.*[5–9] on superalloys. They used test equipment capable of a very high vacuum (1×10^{-8} torr) to study the effect of chemistry, heat treatment and cyclic frequency. The comparative fatigue behaviour in balanced cycling testing in air and vacuum of A286 at 593°C, together with room temperature vacuum test results, are shown in Fig. 1.[5] It is clear that the significant effects of cycle frequency and test temperature in air tests are not found in vacuum tests. Lives may be orders of magnitude less in air, depending on the test frequency. Crack propagation was transgranular for all the vacuum tests and intergranular or mixed, depending on the frequency, for the high temperature air tests.

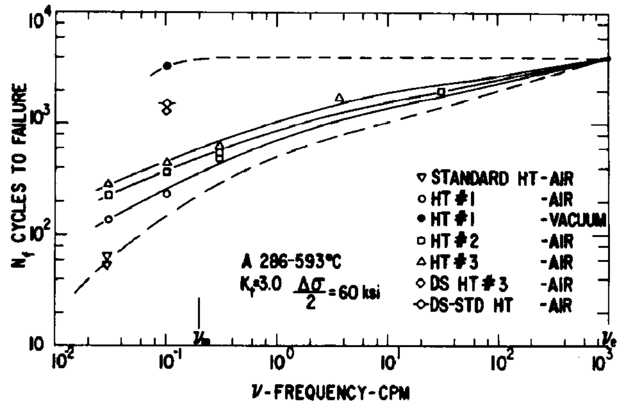
A combination plot for room temperature air and elevated temperature inert atmosphere tests is shown in Fig. 2. The test results are normalised to the plastic strain range for failure at one cycle to establish a common basis for comparison of the slope by eliminating ductility differences. Lines are drawn to show that the Coffin–Manson exponent lies between 0·45 and 0·6. Note that temperatures as high as 1150°C are employed in some of the experiments for which the cycling frequency was ⩾0·2 cpm. This plot normalises all

Table 1 Nominal composition of wrought alloys

Alloy	Ni	Cr	Co	Mo	W	Ta	Nb	Al	Ti	Fe	Mn	Si	C	B	Zr
IN706	41·5	16	0	0	0	0	2·9	0·2	1·8	40	0·2	0·2	0·03	0	0
IN718	52·5	19	0	3	0	0	5·1	0·5	0·9	18·5	0·2	0·2	0·04	0	0
IN625	61	21·5	0	9·0	0	0	3·6	0·2	0·2	2·5	0·2	0·2	0·05	0	0
IN903	38	0	15	0	0	0	3	0·7	1·4	41	0	0	0	0	0
A286	26	15	0	1·3	0	0	0	0·2	2	54	1·3	0·5	0·05	0·015	0
Rene41	55	19	11	10	0	0	0	1·5	3·1	0	0	0	0·09	0·005	0
IN100	55·8	12·4	18·5	3·2	0	0	0	5	4·3	0	0	0	0·07	0·02	0·06
X750	73	15·5	0	0	0	0	1	0·7	2·5	7	0·5	0·2	0·04	0	0
PE16	43	16·5	1	1·1	0	0	0	1·2	1·2	33	0·1	0·1	0·05	0·02	0
MA754	78	20	0	0	0	0	0	0·3	0·5	0	0	0	0·05	0	0
Rene95	61	14	8	3·5	3·5	0	3·5	3·5	2·5	0	0	0	0·15	0·1	0·05
U720	55	17·9	14·7	3·0	1·3	0	0	2·5	5	0	0	0	0·03	0·033	0·03



3 Effect of air and high vacuum on fatigue life of IN706 as function of temperature[6]



4 Effect of frequency on life of notched fatigue bars of A286 at 593°C in air and vacuum[7]

materials independent of test temperature when environmental effects are eliminated.

Figure 3 shows the response of IN706 to testing at a constant plastic strain range and frequency as a function of temperature.[6] This shows a pronounced minimum in life at ~700°C in air tests compared with very little effect on life in vacuum tests over the entire temperature range. The slight minimum in the vacuum tests may imply that truly inert conditions were not achieved, or may indicate a small independent creep damage component. The figure also suggests that the environmental influence may extend to a temperature as low as 400°C. All these data confirm the dominant role of environment in leading to reductions in fatigue lives at high temperatures compared with room temperature tests.

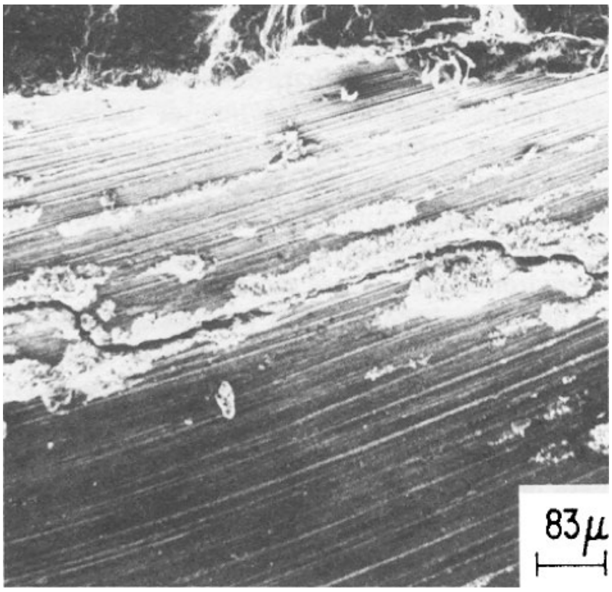
To investigate the effect of cycle frequency and microstructure, fully reversed loading, notched bar fatigue tests of A286 were conducted with three specific aging heat treatments designed to alter the gamma prime precipitate size and the homogeneity of deformation.[7] The results of these tests at 593°C on specimens with a K_t=3, testing at various frequencies, are shown in Fig. 4. A strong frequency dependence of life is apparent below ~5 cpm for all heat treatments. However, the lives are substantially different at a given frequency for the different heat treatments. A double aging treatment (#3) in particular shows much reduced frequency sensitivity than the single lower temperature treatments. Since, for A286, failure at low frequencies was intergranular, elimination of transverse grain boundaries might be expected to increase the fatigue life. Accordingly, two notched specimens were prepared from remelted stock, which had been directionally solidified. Clearly, a substantial improvement was obtained as shown in Fig. 4. If the transverse grain boundaries are retained but the oxygen environment is removed the high vacuum test point indicates a further improvement. The failure of the directionally solidified specimens tested in air to last as long as the vacuum test may be attributed in part to the cast structure in which transverse dendrite boundaries and some transverse grain boundary segments become preferred crack initiation sites. The fracture surface at 30 cpm was largely transgranular and at 100 cpm the life became independent of environment and microstructure.

A damage model was proposed that suggested three regimes: at high frequencies the damage process is independent of frequency and environment; at intermediate frequencies as environmental influence occurs there is a change in fracture mode in air environments from transgranular to intergranular with decreasing frequency; at very low frequencies intergranular fracture may occur even in vacuum.[7] Although the dashed curve through the vacuum point in Fig. 4 is drawn to suggest the onset of this regime at very low frequencies, there was in fact no hard experimental evidence for this. It is always uncertain whether the best vacuum is truly inert at these very low frequencies. This question becomes important for so called creep fatigue interaction considered in a later section. It is also worth noting at this point that, at temperatures >700°C, life should increase with decreasing frequency, based on the temperature sensitivity shown in Fig. 3, and assuming time/temperature kinetics.

Crack initiation

Fatigue crack initiation at elevated temperature usually occurs at a microstructural discontinuity or defect at or near the surface. This may be in the form of machining or polishing markings, brittle phases, voids and grain boundaries (or with cast alloys, interdendritic boundaries).[1] Figure 5 is an example of crack initiation at polishing lines within the notch of a specimen of A286.[7] This specimen was directionally solidified for reasons that are described above. In polycrystalline alloys, cracking may initiate at oxidised carbides and propagate initially along slip band extrusions or directly at grain boundaries as a result of preferential oxidation if the temperature is high enough. Examples for IN706 are shown in Fig. 6.[6] The slip induced initial cracking at lower temperatures will also be influenced by the degree of homogeneous deformation.

The precise way in which cracks nucleate may well be sensitive to the alloy and test conditions. For example, most oxides are brittle and are expected to be a source of initiation, which could then expose fresh metal for



5 Crack initiation at polishing marks in notch root of DS A286 tested in air at 593°C and 0·1 cpm (Ref. 7)

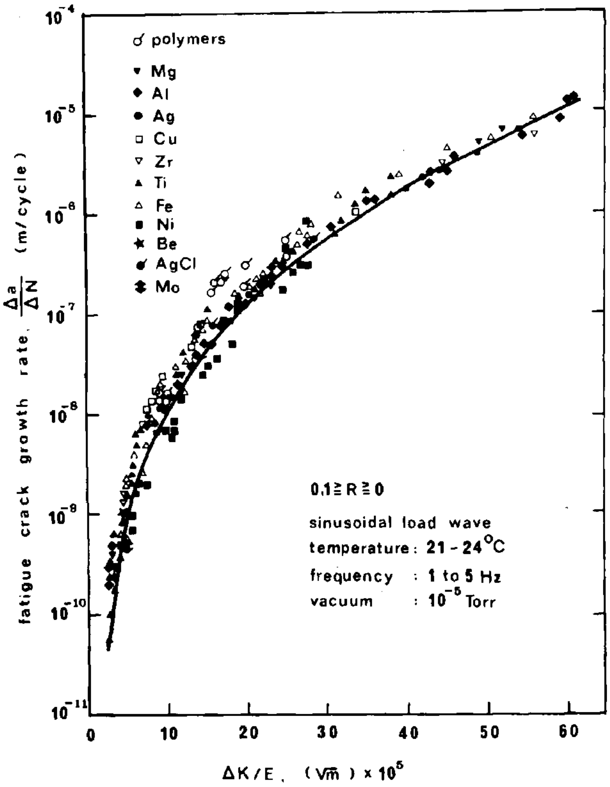
further oxidation. Alternatively, grain boundary oxidation or elemental oxygen penetration ahead of the crack may embrittle the boundary and promote intergranular cracking.[10] Therefore the sequence of events could be important in understanding fatigue cracking and will be returned to in some depth subsequently. All these results relate to air testing at temperatures in the range of about 500°C and upwards; although initiation and propagation are generally transgranular in high vacuum tests, most of the reported vacuum tests are designed to measure crack propagation. It should also be noted that laboratory fatigue tests are normally accelerated by testing at higher temperatures and frequencies than the alloys will experience in service.

Crack propagation

Fatigue crack propagation is generally measured during continuous load cycling of specimens with pre-existing flaws. Differences in crack growth rates for materials tested under cycle dependent conditions (e.g. room temperature in an inert environment) can be explained by differences in elastic modulus.[11] Figure 7 shows cycle dependent crack propagation (CDCP) plotted *v.* the range of stress intensity factor, ΔK, normalised with the elastic modulus, for a wide range of materials. Testing

a 538°C; *b* 649°C; *c* 760°C

6 Examples of crack initiation in air tests of IN706 (Ref. 6)

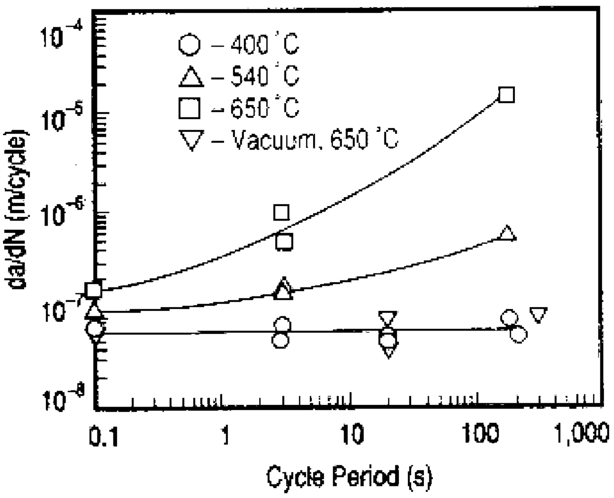


7 Fatigue crack growth rate *v.* modulus normalised stress intensity factor for series of materials[11]

parameters such as cycle period and wave form play a negligible role in determining how fast the crack will grow for a fixed $\Delta K/E$.

The service experience of gas turbines involves low cyclic frequencies, often with long hold times at maximum load and temperature, in an aggressive environment. Under such conditions cyclic crack growth rate is greatly accelerated relative to high frequency effects. Whereas high frequency crack growth is described by fracture mechanics and the crack length is a function only of the number of stress cycles,[12] at low frequencies the crack length is a function of both cycle count and time. In the extreme case where the cyclic frequency is extremely low the crack length may be fully dependent on time and essentially independent of cycle count.[13] The processes that contribute to time dependent crack propagation (TDCP) are thermally activated and therefore become increasingly important with increasing temperature.[14] Figure 8 illustrates these effects in IN718 (Ref. 13). At 400°C the alloy shows pure CDCP at all frequencies with air tests giving the same propagation rates as vacuum tests, but with increasing temperature and cycle period the propagation rates in air becomes more and more time dependent.

Much of the early work assumed that the time dependence stemmed from the nature of deformation at the crack tip and the term creep fatigue was applied.[15,16] However, for nickel based superalloys, the work of Coffin *et al.* demonstrated the dominant role played by the test environment.[5–10,14] The phenomenon is now more generally referred to as creep fatigue environment interaction, although the appearance of pure time dependent fatigue with intergranular fracture in an inert environment (i.e. creep damage as a significant contributor) has not been unambiguously

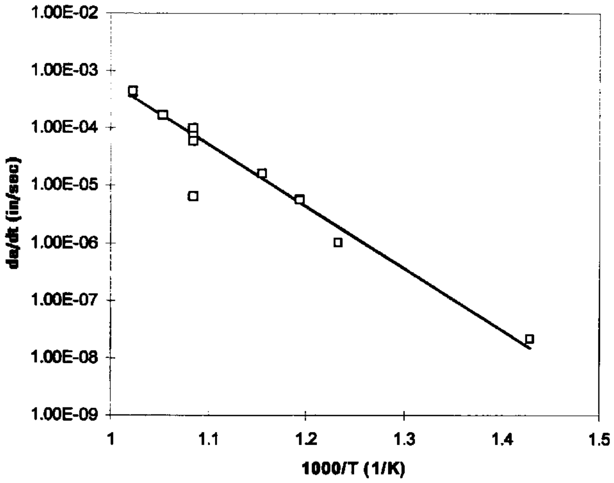


8 **Fatigue crack propagation behaviour in IN718 at ΔK=27·5 MPa m$^{1/2}$ (Ref. 13)**

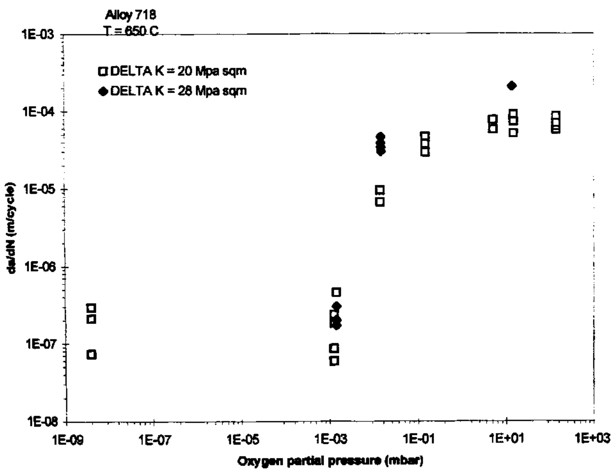
demonstrated. This becomes very important when the author considers both the crack tip physical mechanisms and the models and methodologies on which to base design and life assessment.

In general TDCP of nickel based alloys, for a specific environment, temperature and cycle, can be related to the fracture mechanics parameter of stress intensity in exactly the same way that stable, time independent crack propagation can be, provided net section stresses are low enough that large scale creep can be ignored.[16,17] Crack growth rates for IN718 have been measured over a range of temperatures in air by many authors[17–23] and combined in the Arrhenius format (Fig. 9) for K_{max}=30 MPa m$^{1/2}$ yielding an activation energy of 206 kJ mol^{-1} (Ref. 24). These data extend to a low temperature of 425°C.

It is generally believed that the damaging species in air is oxygen. This has been substantiated for a few alloys by measuring crack propagation rates or cycles to failure (for LCF testing) as a function of oxygen pressure for a given cycle period and stress intensity factor range or strain range (for LCF). These studies involved establishing a high chamber vacuum and then using a leak valve to control oxygen pressure. The results of Andrieu *et al.*[25] from such an experiment



9 **Sustained load crack growth rate (d*a*/d*t*) *v.* reciprocal temperature for IN718 at K_{max}=30 MPa m$^{1/2}$ (Ref. 24)**



10 **Fatigue crack growth rate as function of oxygen pressure at constant ΔK at 650°C in IN718 (Ref. 25)**

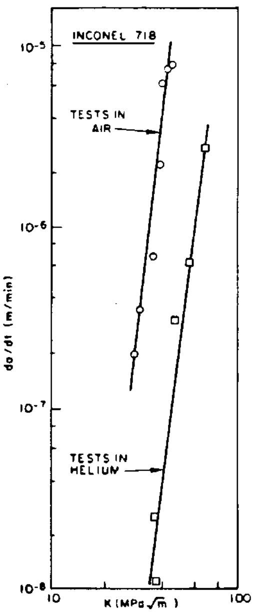
are shown in Fig. 10. Between pressures of about 1×10^{-1} torr and 1×10^{-3} torr the crack propagation rate dropped by three orders of magnitude. At both higher and lower pressures than the transition range the crack growth rates were nearly constant.

Although it has been known for some time that sulphur containing environments may be more damaging than oxygen containing environments,[26] recent work[24] has shown that there may also be very substantial effects of water vapour on the kinetics of crack growth. This work will be considered in more detail subsequently.

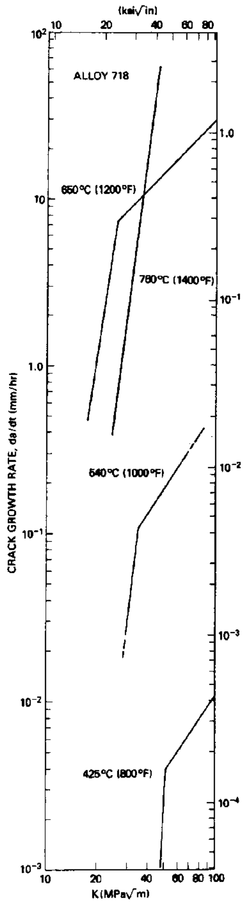
Sustained load crack propagation

Subcritical crack growth in the temperature range where creep occurs has been called creep crack growth. However, in keeping with the author's stated aim to avoid terms that imply mechanisms, and also to recognise that environment may again have a dominant effect,[26] sustained load crack propagation is the preferred term. Creep crack growth might be reserved for time dependent subcritical crack growth in an inert environment. Figure 11 shows that at 650°C the crack growth rate for IN718 is ~100 times slower in helium than in air,[26] and Fig. 12 shows the strong temperature dependence of crack growth rate in air.[27] Crack growth was observed at a temperature as low as 425°C at high values for K>50 MPa m$^{1/2}$. The reduction in crack growth rate at 760°C was attributed to increased plasticity relative to 650°C and a reduction in yield stress. More recent studies on IN718 have reported sustained load crack growth rates in oxygen at 700°C to be >10 000 times faster than in high purity helium.[28,29]

Very strong effects of microstructure on sustained load cracking in air have been reported for both IN718 (Ref. 30) and, recently, for IN706 (Ref. 31). In the latter case it was found that a typical direct aging (DA) treatment producing fine gamma prime/gamma double prime precipitates led to crack propagation rates of 0·1 mm h^{-1} at stress intensities as low as 30 MPa m$^{1/2}$ at 600°C. A modified stabilisation heat treatment (MST), including controlled cooling, produced a reduction in crack growth rate of about two orders of magnitude. Although questions remain regarding in-service microstructural stability, this work demonstrates a tremendous potential for increasing resistance to



11 Sustained load crack growth of IN718 at 650°C as function of *K* (Ref. 26)



12 Effect of test temperature on sustained load cracking in IN718 (Ref. 27)

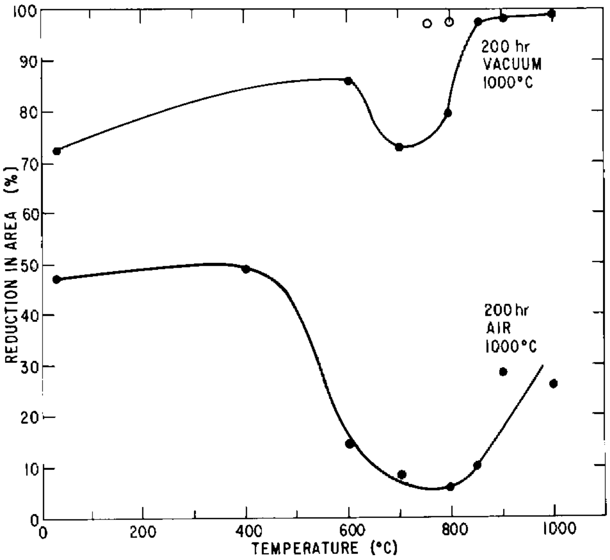
sustained load cracking of IN706 in hostile environments. It should also be recognised that creep strength, strain capability, elastic modulus and the way these properties are controlled by precipitate size and distribution, grain size and orientation are all expected to influence crack propagation and the interaction with the environment.[32]

Fixed displacement load relaxation tests on single edge notch (SEN) specimens have been used to show that sustained load crack growth rates in IN718 at 650°C are extremely sensitive to oxygen pressure.[33] The oxygen induced cracking was discontinuous, and the interruptions were marked by striation-like steps on the intergranular fracture surface. The process was referred to as dynamic embrittlement, which led to a proposed mechanism, to be discussed subsequently. The idea of a dynamic embrittling process occurring at the tip of a crack is appropriate and will subsequently be used for both cyclic and sustained load crack propagation. It should be contrasted with the well known process of environmentally induced embrittlement occurring during exposure at high temperature in the unstressed condition,[10] which will be referred to as static embrittlement.

Static embrittlement

It was demonstrated many years ago that gases could penetrate large distances into polycrystalline nickel by preferential grain boundary diffusion,[34] and that this could lead to a degradation of tensile and creep ductilities.[35,36] The phenomenon of oxygen penetration was studied extensively in the seventies and eighties.[10] It was shown that many nickel, iron and cobalt superalloys were susceptible. The extent of damage and penetration increased with increasing time and temperature, but the amount of degradation of tensile ductility and creep life was a maximum at intermediate temperatures. There was a strong sensitivity to composition. It was found, for example, that high chromium levels, either in the alloy or present in protective coatings, could reduce the oxygen activity (or partial pressure) sufficiently to prevent penetration and that boron additions could actually reduce the grain boundary diffusivity of oxygen. To understand the mechanisms and measure the kinetics, much of the work was done on various grades of nickel and specially doped simple alloys. This work and some relevant studies of wrought and cast nickel based alloys are described as a framework to address the question of the commonality of mechanism with the dynamic embrittlement that occurs in advance of a propagating crack.

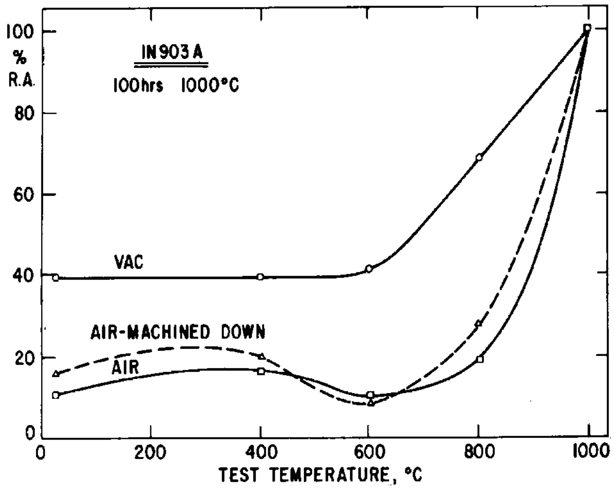
Figure 13 shows the tensile ductility, measured as a percentage reduction in area, for Ni270 (a commercially pure grade of nickel) at various temperatures following 200 h exposure in either air or vacuum; testing was performed in vacuum. There is a drastic loss in intermediate temperature ductility after air exposure. The restoration of ductility at temperatures above ~800°C may be related to the minimum in fatigue life as a function of temperature shown in Fig. 3 for the dynamic embrittlement during fatigue of IN706. The small minimum that developed after vacuum exposure is apparently eliminated for the two specimens that were vacuum exposed before machining from a large block. By exposing in nitrogen, carbon dioxide, carbon monoxide and oxygen it was demonstrated that oxygen was the embrittling species. Embrittlement occurred after exposure in a Ni–NiO pack, which produces an oxygen partial pressure of $<1\times10^{-7}$ torr, and allows no stable NiO scale to form. Moreover, embrittlement was prevented for specimens that were coated with an



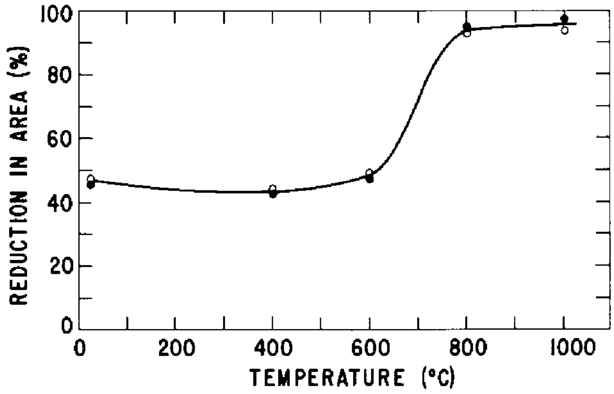
13 Effect of air and vacuum exposures for 200 h at 1000°C on tensile ductility in vacuum of Ni270 as function of test temperature[37]

aluminised layer or a plasma sprayed CoCrAlY coating before air exposure.[37]

The embrittlement is shown strikingly in the fractographs of Fig. 14 for similar experiments on Ni200 (a less pure grade of nickel).[38] The vacuum exposed specimen necked down to a point (Fig. 14*a*), whereas total intergranular fracture resulted after air exposure (Fig. 14*b*). In this example, a well defined external shell corresponding to the depth of matrix internal oxidation of impurity elements (250 μm) can be observed. The question arose as to whether embrittlement was limited to this zone of internal oxidation; intergranular fracture of this zone might then force the crack to continue in a quasi-brittle mode. To resolve this question, a specimen was exposed in air under the same conditions and then the gage diameter was reduced to 1·25 mm, therefore removing more than twice the thickness of the internally oxidised zone. The fracture was intergranular as before (Fig. 14*c*) with a reduction in area of only 13%. Therefore it was demonstrated that intergranular embrittlement occurred far in advance of matrix internal oxidation. This was confirmed with a series of similar experiments on IN903A shown in Fig. 15 (Ref. 39) and on many other tested alloys, including IN706 (Ref. 10).

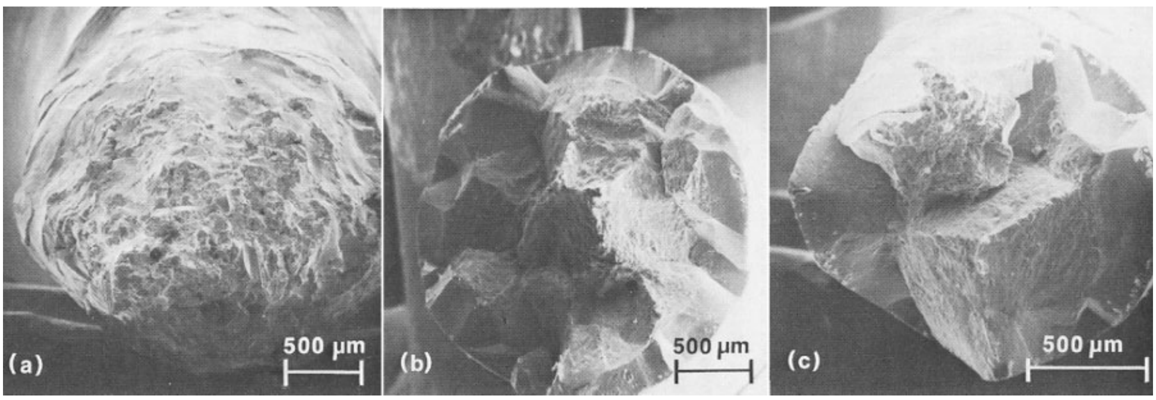


15 Ductility of IN903A after air and vacuum exposures at 1000°C as function of test temperature in vacuum tests: embrittlement remained after reducing to half initial diameter[39]



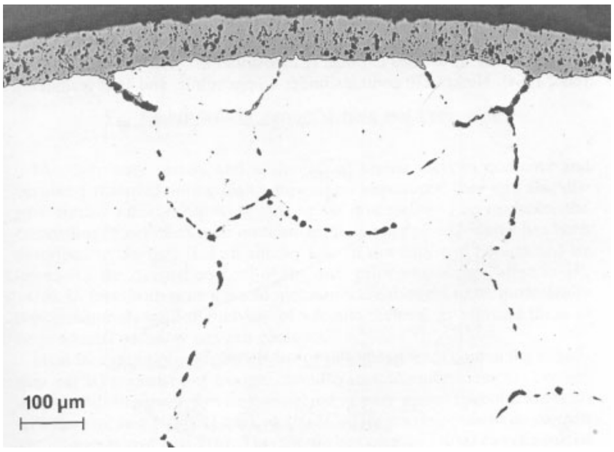
16 Tensile ductility of Hastelloy X as function of temperature for specimens exposed at 1000°C before testing in vacuum: filled symbols, air exposed; open symbols, vacuum exposed[10]

However, some alloys showed little or no sensitivity. The results for the high chromium alloy (22%), Hastelloy X, are shown in Fig. 16. This alloy forms a stable adherent chromium oxide scale and prevents oxygen penetration. The result should be compared with the effect of chromium level on fatigue crack propagation in modified IN718. The time dependent crack

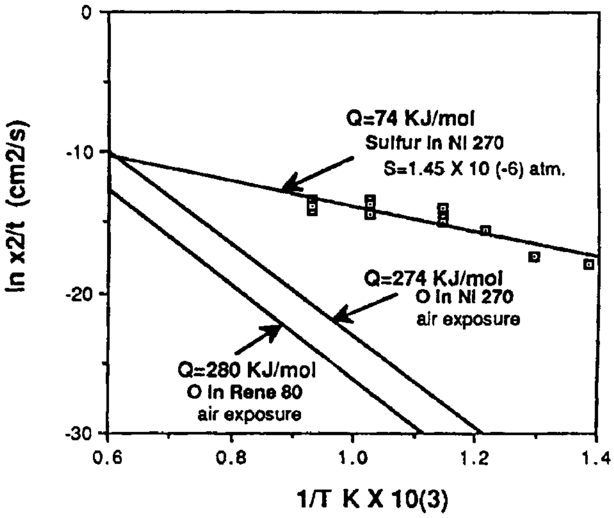


a vacuum exposed: ductile transgranular rupture; *b* air exposed: intergranular fracture showing ring of internal oxidation; *c* air exposed and machined to half diameter before testing: intergranular fracture

14 Fracture surfaces of Ni200 at 800°C after treatment at 1000°C (Ref. 38)



17 External oxide and internal voids formed in Ni270 after air exposure at 1000°C for 200 h (Ref. 37)



18 Plot of oxygen penetration in Ni270 and Rene 80 and sulphur penetration in Ni270 (Ref. 50)

propagation at 540°C was eliminated at chromium levels of 24% (Ref. 13).

Besides high chromium levels it was shown that additions of boron, zirconium and hafnium were beneficial in reducing oxygen embrittlement in various alloys. Degradation was measured either by tensile ductility or stress rupture life.[40] By doping nickel with boron it was shown that no intergranular oxides beyond the region of matrix internal oxidation were observed. This suggested that boron was effective by occupying the grain boundary sites used by oxygen for rapid diffusion and therefore blocking its penetration down grain boundaries. Possibly the large atoms, Hf and Zr, and the small atom, B, which are all grain boundary segregants, play similar roles in inhibiting interstitial diffusion of oxygen down grain boundaries. Together, they might be even more effective. However, Hf and Zr also serve as getters for impurity sulphur, which segregates from the grain interiors. Recent work has demonstrated that additions of boron and magnesium reduce tensile embrittlement during air testing in IN706 (Ref. 41).

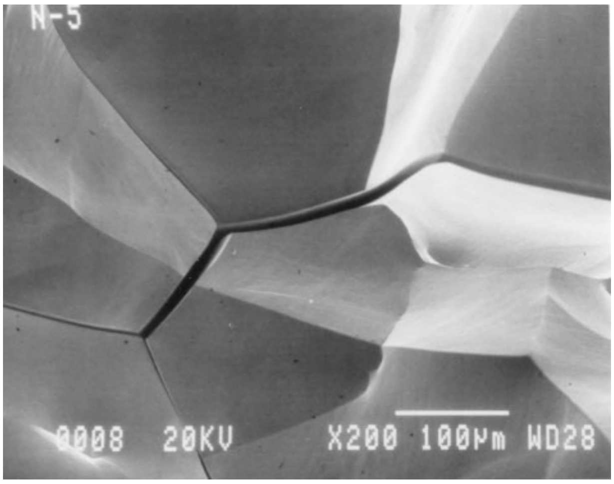
Having demonstrated that intergranular oxygen penetration leads to embrittlement, often with a maximum sensitivity at intermediate temperatures, in nickel and its alloys, it was appropriate to examine the mechanism. It was first established that oxygen did not embrittle in high purity nickel by decarburising Ni270 (using a hydrogen anneal) before air exposure.[42] It therefore appeared that an oxidation reaction was necessary and that oxygen did not embrittle in the elemental form, at least in pure nickel. The first clue to the nature of the reactions that might be involved was the role of carbon. In the presence of carbon, oxidation led to what appeared to be cavity development in near surface grain boundaries. An example is shown in Fig. 17. Such voids had previously been attributed to vacancy injection from the growing oxide,[35,36] or to creep induced cavities where the creep stress arose from the volume mismatch between scale and metal.[43] However, it was shown unambiguously, using mass spectroscopy of intergranular fractures in vacuum, that these voids are in fact gas bubbles and most likely carbon dioxide, possibly with some carbon monoxide.[44] This was subsequently confirmed on the basis of thermodynamic calculations.[45] Exposure of some nickel based alloys to high temperature air causes similar near surface gas bubble formation.[46]

Another type of reaction that can occur is a chemical reaction leading to the release of other embrittling species. For example, oxidation of grain boundary sulphides releases sulphur, which does embrittle in the elemental form.[47] Finally, in the absence of carbon or sulphides in nickel it was found that intergranular internal oxidation of trace impurities, or of deliberately added oxide forming dopants, occurred.[48] This was detected far in advance of the matrix internal oxidation.

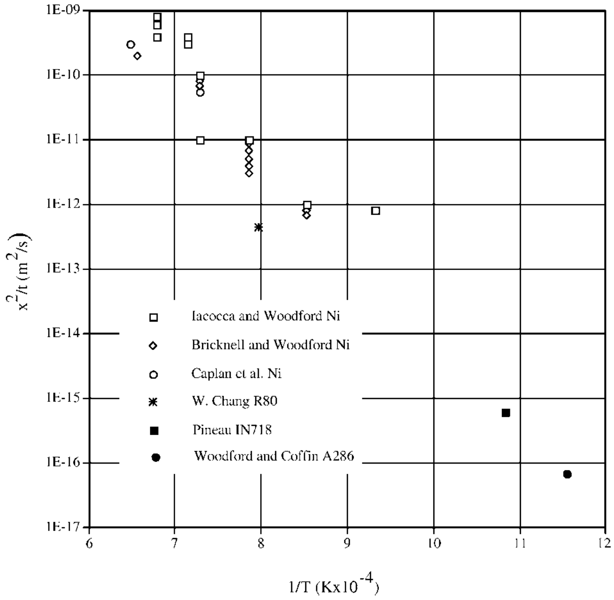
At least four processes appear to be germane to grain boundary oxygen embrittlement: gas bubble formation, release of sulphur following oxidation of sulphides, precipitation of alloy oxides and finally solute segregation. The author includes the latter because, although oxygen does not appear to embrittle nickel in the elemental form, it is possible that it might affect the cohesive strength of grain boundaries in intrinsically less ductile alloys.

In the present section, it should also be mentioned that exposures to sulphur and chlorine vapour actually embrittle nickel more severely than does oxygen, after exposure at 800°C (Ref. 49). A systematic study of the effect of sulphur partial pressure on the temperature dependence of tensile embrittlement in Ni270 showed that for exposures between 450 and 900°C, a maximum embrittlement was observed at $\sim$700°C. Partial pressures of sulphur exceeding $\sim 1 \times 10^{-5}$ torr were embrittling. Kinetic measurements, based on the depth of post exposure intergranular fracture, gave an activation energy of 74 kJ mol^{-1} in the temperature range 450–800°C. This value is considerably less than the value reported for matrix sulphur diffusion and also less than that for intergranular oxygen diffusion as shown in Fig. 18 (Ref. 50). In this Figure oxygen penetration in Ni270 was determined from the depth of gas bubbles or intergranular internal oxidation. Oxygen penetration in the cast nickel based alloy, Rene 80, was determined from the amount of material it was necessary to remove to restore ductile transgranular fracture.[51]

Grain boundary fracture following sulphur exposure indicated decohesion at smooth interfaces with no evidence of chemical reactions (Fig. 19). This



19 Grain boundary decohesion in Ni270 after sulphur exposure[51]



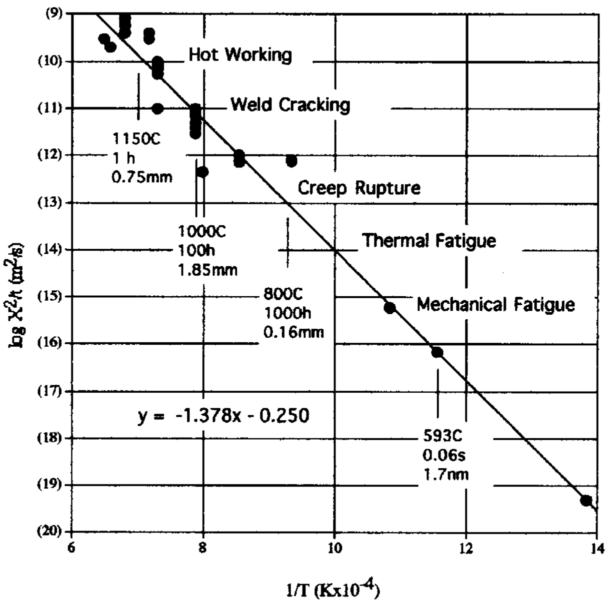
20 Intergranular oxygen penetration as function of test temperature

appearance is quite different from the intergranular fracture shown in Fig. 2 after air exposure. The lowest temperature of sulphur embrittlement, 450°C, is well below the melting temperature of any known nickel sulphide. The evidence was, therefore, compelling that the cause of sulphur embrittlement is elemental diffusion of sulphur down grain boundaries. Other chalcogens (Se, Te) and the halogens (F, Cl, Br, I) as well as metal vapours (Pb, Bi) may undoubtedly lead to gas phase embrittlement (GPE).

Although decohesion is a probable cause of the embrittlement for sulphur, and perhaps some other gaseous species, oxygen apparently does not lead to decohesion as noted above, but rather induces an intergranular fracture as a consequence of a chemical reaction affecting the process of grain boundary separation. An indication of the mechanism by which an oxidation process on the grain boundary (other than sulphur release) affects ductility was afforded by the load time curves of air and vacuum exposed nickel tested at the temperature of the ductility minimum. That of the vacuum exposed specimen showed the oscillations characteristic of dynamic recrystallisation whereas the air exposed specimen displayed none.[37] It was also shown that air exposed material displayed a greater resistance to recrystallisstion at 800°C following cold work. Therefore a link between boundary mobility and embrittlement was established. This link can be explained in the following manner. At low temperatures the deformation is carried by slip with little or no grain boundary sliding. At intermediate temperatures grain boundary sliding occurs and is accommodated by slip in the near boundary regions. The resulting dislocation tangles or pileups produce stress concentrations and limit further accommodation. However, these may be reduced by grain boundary migration allowing for continuing slip and accommodation. By contrast, in oxygen embrittled specimens migration is hindered, further accommodation is prevented, and cracks initiate. At the highest temperatures the boundaries gain enough thermal energy to break away from this pinning, accommodation once again occurs, and ductility is restored. This reasoning can therefore explain a tensile ductility minimum, as shown in Fig. 13 and, possibly, the fatigue life minimum as shown in Fig. 3. Therefore, oxygen embrittlement may be regarded as arising from a boundary immobilisation by oxides or gas bubbles leading to the prevention of accommodation for grain boundary sliding rather than an intrinsic reduction in grain boundary cohesion. This is in agreement with the general observation that oxygen embrittlement leads to no change in yield strength. This line of argument can also explain the lack of degradation seen in the oxide dispersion strengthened alloy, MA754, on air exposure.[52] It is reasoned that this alloy has its boundaries pinned by oxides, has low starting elongations in the midtemperature range, and can be regarded as intrinsically embrittled.

Finally, in the present section kinetic measurements of oxygen penetration are applied to determine whether these same mechanisms could explain fatigue and sustained load cracking in oxygen containing environments. Figure 20 shows data for oxygen penetration in Ni270 measured by the depth of gas bubble or intergranular internal oxidation, in Rene 80 measured from surface machining experiments, and from IN718. In the latter case specimens were fatigue precracked at room temperature, exposed in air at 650°C and then tensile tested in argon. The initial intergranular cracking observed was a measure of oxygen penetration that had occurred during the exposure. It should also be noted that the single point plotted for Rene 80 represented the best fit through 29 points for various exposure times at 982°C (Ref. 51). Also, in this alloy, as in many of the model materials, the depth of intergranular penetration was more than an order of magnitude greater than the thickness of surface oxidation. A regression curve was then plotted through all the data points and is shown in Fig. 21.

The data used for the curve fit represent all results taken from static embrittlement experiments. An additional point was then placed on the line to determine whether similar kinetics might apply for dynamic embrittlement. The data point labelled Woodford and Coffin[7] uses Fig. 4 and the frequency beyond which the fatigue life is time (or frequency) independent. At the

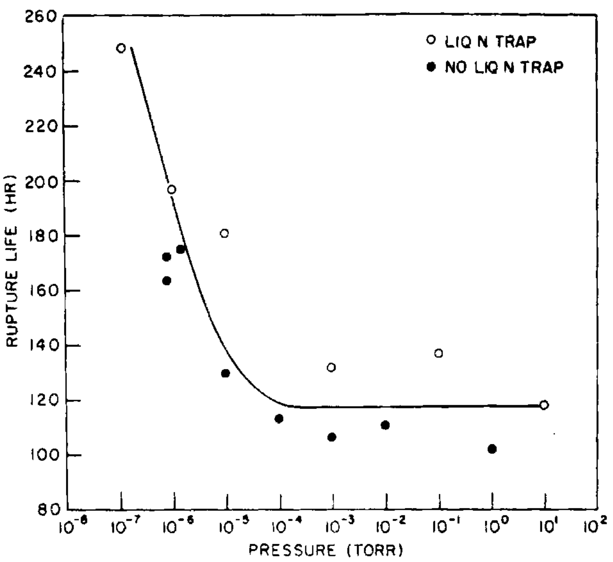


21 **Oxygen penetration curve showing ranges for specific interactions**

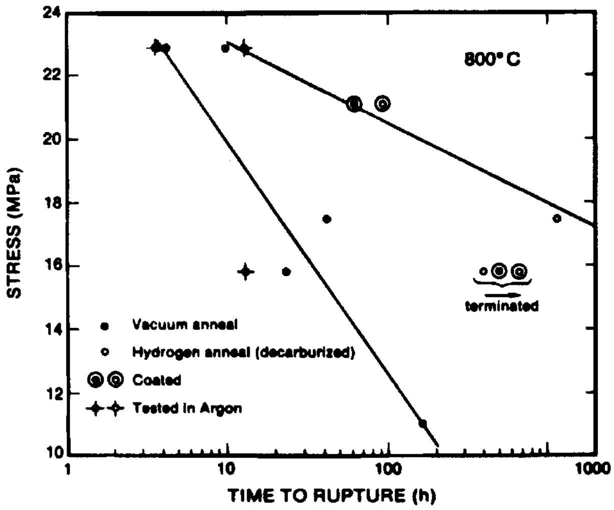
temperature of 593°C, the cycle time of 0·06 s corresponds on the fitted line to a penetration depth of ~2 nm, i.e. on the order of a few atom spacings. This result for the fatigue data is reasonable, i.e. it is to be expected that the limiting damage should be on the order of the atomic spacing. The result also implies that there is no major acceleration of oxygen diffusion under cyclic stress.

Environmental enhanced creep fracture

This is the fourth in the relevant streams of investigation and is restricted to crack initiation and propagation in uncracked bodies, i.e. creep fracture of smooth or notched specimens. Early work on high purity copper showed a time dependent embrittlement that was much more rapid when tested in air than in argon.[53,54] The first systematic study of the effect of oxygen pressure



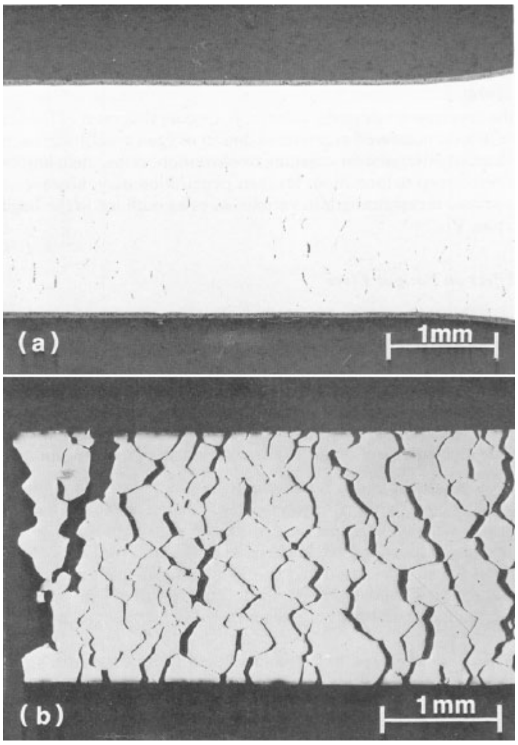
22 **Creep rupture life of nickel as function of oxygen pressure at 600°C and 58·6 MPa (Ref. 55)**



23 **Stress rupture results on Ni270 at 800°C showing influence of oxygen/carbon reaction in leading to reduced lives: testing in air except where indicated[56]**

was done on commercially pure nickel.[55] Figure 22 shows that there was a sharp increase in rupture life, corresponding to an increase in ductility below a pressure of 1×10^{-4} torr. The depth of intergranular surface cracking increased with increasing oxygen pressure. Recall that there was a sharp decrease in fatigue crack growth rate in IN718 at 1×10^{-3} torr (Fig. 10). This provides evidence that intergranular failure from a sharp crack in fatigue is controlled by the same environmental interaction process as rupture life of a smooth specimen.

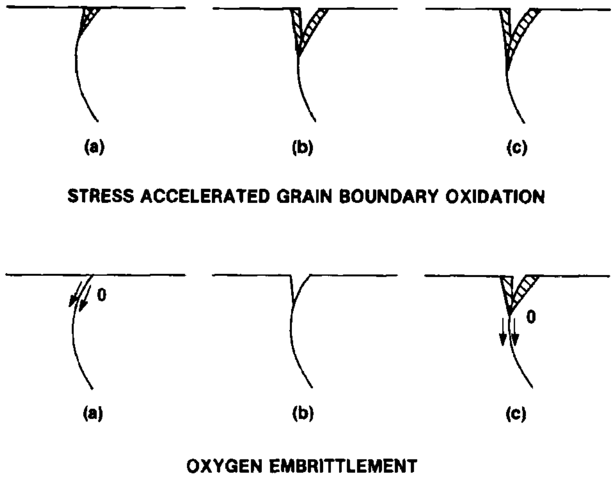
To explore the possible link between static embrittlement and creep fracture a series of creep rupture tests were run on nickel in ways that allowed or disallowed the carbon/oxygen grain boundary reaction. The results shown in Fig. 23 indicate two populations of rupture lives.[56] Specimens that were hydrogen annealed (carbon removed) or coated (oxygen could not enter) had much longer lives. Specimens that were vacuum annealed and tested in air or argon showed short lives and massive intergranular cracking. The argon is clearly not inert under these test conditions and, based on a necessary vacuum of better than $1{\cdot}33\times10^{-2}$ Pa to improve on air (Fig. 22), which is equivalent to an impurity level of only 0·13 ppm of oxygen in the argon, it is not surprising. Figure 24 shows metallographic examples[57] of the effect of allowing the gas bubble formation to occur in the carbon containing Ni270. Therefore creep cavitation in nickel is a direct consequence of the gas bubble formation first examined for static oxidation. This establishes the link between static embrittlement and environmental enhancement of creep fracture. The inference is that the other embrittling processes (i.e. intergranular oxide formation, and release of sulphur from oxidised sulphides) identified in static embrittlement could also lead to accelerated creep fracture. Recalling the evidential link between the oxygen pressure sensitivity in the failure of a cracked and uncracked body, the author now has established a common mechanistic basis for all four experimental streams, namely static embrittlement, dynamic embrittlement in cyclic and sustained loading, and stress rupture of smooth specimens.



a low carbon Ni270 onloaded after 500 h: slight cavitation; *b* standard Ni270 after failure in 23 h
24 Unetched microstructure of nickel specimens after air testing at 15·8 MPa and 800°C (Ref. 57)

It should be noted that many authors have observed that intergranular cracking in creep tests of engineering alloys invariably initiate at the surface. In austenitic steels it was also found that this cracking is far less extensive in vacuum tested specimens.[58] The sensitivity to this oxygen enhanced cracking is often increased in notched specimens. In developing the chromium free Fe–Ni based low coefficient of expansion alloy, IN903, the term stress accelerated grain boundary oxidation (SAGBO) was coined[59] to describe this phenomenon. Unfortunately, the term has come to be used extensively and generally to describe environmental enhancement of elevated temperature failure of engineering alloys, even though it implies a mechanism of successive oxide cracking. Figure 25 compares this mechanism with gas phase embrittlement by oxygen. SAGBO assumes preferential oxidation at grain boundaries and cracking of the oxide, which exposes new surface for further oxidation and subsequent cracking. It should be insensitive to the type of oxide. Oxygen embrittlement, which is a specific example of GPE, does not require the presence of an oxide scale but should be sensitive to oxygen partial pressure, and will advance well beyond any oxide scale. The oxidation always occurs in the wake of cracking and the boundary is embrittled beyond the crack tip and any surface scale. The observations described above clearly favour GPE as the source of crack enhancement. Intergranular oxygen penetration, provided the partial pressure of oxygen is high enough to promote environmental acceleration of crack propagation, is typically more than an order of magnitude deeper than any oxide scale, as noted previously.

Recent work on creep rupture of notched and smooth specimens of IN718 and IN909 also concluded that SAGBO was not a viable mechanism to explain early intergranular fractures.[60] This paper includes as a co-author the principal author of the first SAGBO paper.[59] In fact, the later work reported that oxygen embrittlement was enhanced by high moisture content in the test furnace air, and postulated that this served to increase the kinetics of oxygen diffusion down grain boundaries. The role of water vapour is an important factor, which will be considered in somewhat greater detail subsequently.

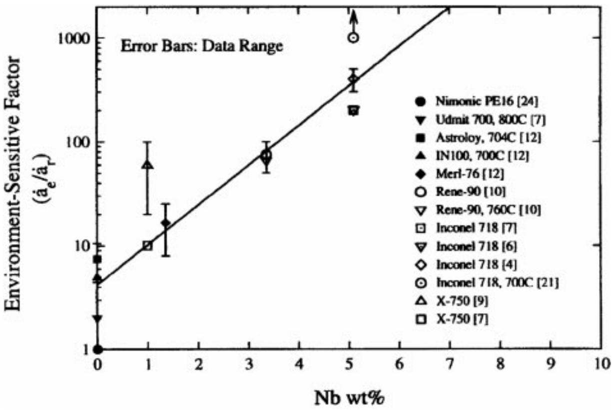


25 Comparison of SAGBO and oxygen embrittlement processes of crack propagation

Crack tip oxygen embrittlement

In the previous sections the authors have attempted to illustrate similarities in the characteristics and kinetics of GPE by oxygen in leading to both dynamic and static embrittlement. There is a critical partial pressure of oxygen below which there is no time dependent cracking or embrittlement. For all types of dynamic embrittlement, and for static embrittlement, direct intergranular diffusion of oxygen is the dominant process. Unlike several other species, including sulphur, oxygen does not appear to embrittle in the elemental form. In special circumstances sulphur may be released as a result of the oxidation of grain boundary sulphides, which could then lead to intergranular decohesion. However, the more common reactions include gas bubble formation as a result of oxidation of carbon or carbides, and the oxidation of impurities or minor alloying additions. Although the former can act as creep cavity nuclei and directly lead to intergranular fracture, both types of reactions will reduce the ability to relieve stress concentrations at sliding grain boundaries. The temperature and time dependence of the sliding and accommodation processes can explain the maximum in temperature sensitivity to cracking at intermediate temperatures.

There are two interpretations of time dependent cracking that might challenge the above interpretation. One is based on the progressive cracking of an intergranular oxide scale.[59] This may be refuted on the basis that an oxide scale is not a necessary condition for accelerated crack propagation or static embrittlement, although the process might be involved in the initiation stage of high temperature fatigue. The second is the idea of a plating of oxygen atoms driven under tensile stress from the surface to the crack tip.[33] This process also



26 Ratio of crack growth rates in air to those in vacuum or argon as function of niobium concentration:[62] testing at 650°C except as indicated

might be involved to some degree. However, it was postulated to be the principal source of intergranular cracking in IN718 even though local oxidation fronts on the fracture surface[33] suggest normal diffusion processes on a small scale at the crack tip. The finding that high purity nickel does not embrittle[42] indicates that intergranular diffusion and subsequent oxidation reactions are required. In fact the stepped form of the sustained load crack propagation on a fine scale[33] could be used to support the idea of a local sequence of grain boundary sliding and migration.

There have been an enormous number of phenomenological studies of all major classes of engineering alloys in many gaseous environments.[61] Understanding the nature of the local interactions is still a major challenge. The interaction of oxygen with the tip of a propagating crack is extremely difficult to study microstructurally because of the small scale penetration involved at temperatures of interest (i.e. 400–650°C). In the present paper the authors have drawn heavily on the associated observations of static embrittlement, in which much greater damage penetration distances are involved, to reach some conclusions. Nevertheless, there have been several attempts to examine the crack tip region in detail. Wei *et al.*[62] have examined the region ahead of sustained load cracks in IN718 and noted strong concentrations of niobium at the grain boundaries as a result of oxidation of niobium carbides. They showed a correlation between environmental sensitivity and niobium content for several alloys (Fig. 26). However, in a later paper they conceded that significant oxygen enhanced cracking occurred in a niobium free alloy.[63] It is not clear whether niobium is a fundamental factor in the mechanism, e.g. by forming intergranular metallic oxides, or whether it affects the microstructural sensitivity and creep strength.

A recent detailed study of crack tip oxides in IN718 and IN706 showed complex oxides of nickel and chromium, but no features that could be correlated with a damage zone ahead of the crack tip.[64] This was confirmed in a comprehensive study of IN718 in which it was also shown that the presence of a crack destabilised chromia formation when sufficient concentrations of oxygen or water vapour were present in the bulk atmosphere.[24] Test environments that were associated with the formation of Ni, Fe and Co rich oxide scales were found to be associated with accelerated time dependent crack propagation.

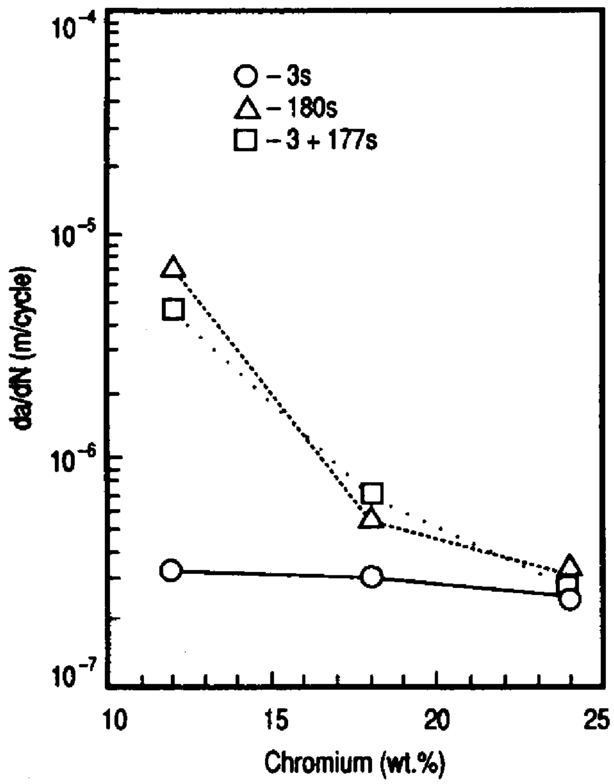
The idea of a damage zone ahead of a propagating crack tip has been taken up by many authors in the last half century. There have, however, been no direct microstructural observations, which is not surprising because it is likely that the authors are dealing with a few atom distances. Attempts to measure such a zone based on electrical potential crack growth rates[65] using a frequency change experiment led to estimates of damage zones on the order of a millimeter. These measurements, when duplication was attempted, were later shown to be a characteristic of the potential difference measuring technique.[24] Nevertheless, the concept of a much smaller damage zone which is dependent on the crack tip thermal–mechanical profile is an essential part of the analysis of time dependent crack growth rates and will be considered in a subsequent section.

The last item considered in this section is the role of water vapour. Most experiments to control oxygen pressure have used controlled leak rates in a high vacuum.[25,66] However, an alternative approach is to use a controlled mixture of hydrogen, water vapour, oxygen and argon.[24] Both oxygen and water vapour were found to have independent influences in promoting time dependent cracking of IN718 at 593°C. No specific explanation was offered in terms of the effects of water vapour on oxidation kinetics or on a possible separate role of hydrogen. Although there is a long history of the harmful effects of moisture on fatigue in many engineering alloys,[61] this area has seen little systematic attention in superalloys.

One interesting study of the effect of annealing environment on the cracking of a Fe–28Cr–10·5Co magnet alloy in subsequent bend testing showed that wet argon, wet nitrogen, wet air and dry hydrogen led to cracking. By contrast there was no cracking after annealing in dry argon, nitrogen, air and oxygen.[67] There was no indication of static oxygen embrittlement here, which is consistent with the very high chromium content. Clearly, moisture in this case leads to hydrogen embrittlement. The ductility was fully restored after a hydrogen relief treatment at 250°C. Therefore the strong effect of water vapour on fatigue cracking at 593°C in IN718 (Ref. 24) implies that a reaction, possibly methane formation by reaction of hydrogen with carbides, or a synergistic effect with oxygen in which the hydrogen prevents the formation of nickel oxide, is involved. It is also appropriate to recall the discussion of the effect of moisture on creep rupture cracking of superalloys.[59] The increasing use of steam cooling in industrial gas turbines has rendered this a very important topic. However, apart from the work noted above, little information is available on the effect of water vapour on dynamic cracking of superalloys in the open literature.

Role of chemistry and microstructure

Although it is clear that time dependent intergranular cracking at elevated temperatures is principally, and perhaps exclusively, a result of testing in a non-inert environment, the sensitivity to environmental interaction can be reduced or, in some cases, eliminated by chemistry or microstructural control. This is a vast



27 Effect of chromium on fatigue crack growth rate in IN718 at 540°C with ΔK=30 MPa m$^{1/2}$ (Ref. 13)

subject with multiple opportunities available for influencing the fatigue lives of any alloy. Also, since most testing is conducted in air, the general observations relate primarily to the situation where oxygen is the damaging species. The authors consider below some established principles for improving fatigue lives of superalloys at elevated temperatures.

Alloy chemistry

Figure 27 shows the beneficial effect of chromium level in reducing the time dependent cracking in modified IN718 compositions.[13] The strength was maintained by replacing chromium with iron, and the higher frequency (3 s cycle) crack growth rates were independent of chromium content. However, for the 180 s periods there was a strong effect of chromium such that at a 24% level there was no time dependence for the cycle conditions studied. Recall that commercial IN718 has a nominal concentration of 18·5% chromium.

Other elements that have been found to be beneficial are boron, zirconium and hafnium. These elements have long been known to be beneficial to the creep rupture and sustained load crack growth behaviour of superalloys[68,69] and are believed to minimise the deleterious effects of oxygen. They may act to inhibit intergranular oxygen penetration by occupying grain boundary sites as small (B) or large (Zr, Hf) atoms. Although there is direct evidence for boron reducing intergranular oxygen penetration in nickel,[48] zirconium and hafnium may also play other roles. They act as strong getters for sulphur and carbon. By removing these elements from the grain boundary regions they are expected to prevent two of the observed harmful reactions of oxygen in the grain boundaries.[10] A cast alloy, IN738, was found to be less susceptible to brittle intergranular stress rupture after prior air exposure (static embrittlement) when the carbon was replaced with boron or when 1·5% hafnium was added.[40]

Some effects of trace impurities may promote embrittlement without having a direct interaction with oxygen damage. It is well known[70,71] that lead, selenium, tellurium, arsenic, bismuth, as well as sulphur may embrittle directly by segregating to grain boundaries from the grain interior. Phosphorus[72,73] has been shown to be beneficial in stress rupture life and ductility of IN718. In IN706, magnesium as well as boron has a direct beneficial effect on oxygen induced intergranular cracking.[74] In IN718, niobium is the primary carbide former and consequently is released at the grain boundaries as a result of oxygen penetration.[62] It may not be especially harmful as a segregating element but oxidation of the carbides releases carbon, which can then react to form gas bubbles.

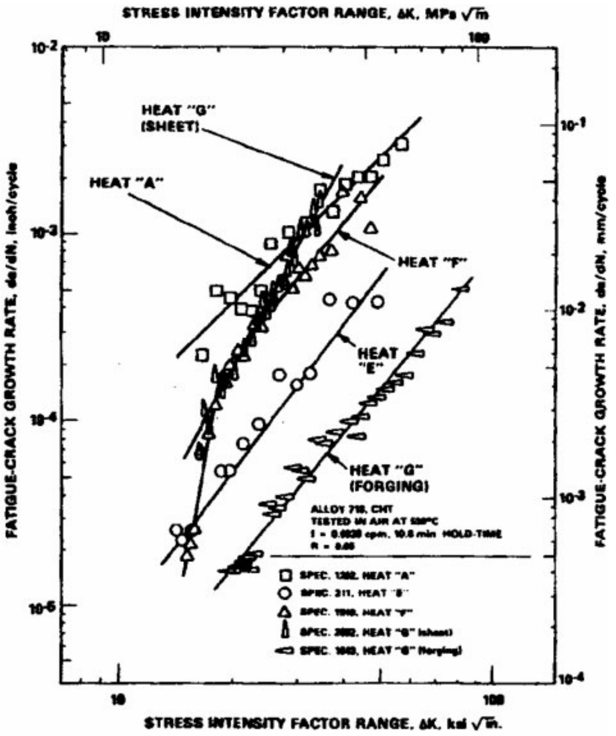
Attempts have been made to interpret the effects of trace elements on intergranular fracture in terms of their effects on grain boundary sliding, and associated migration to accommodate the resulting stress concentrations. Other suggestions include effects on interfacial energy controlling cavity nucleation. Although the evidence is largely circumstantial,[75] these arguments are consistent with our general interpretation of oxygen enhanced intergranular cracking in superalloys. In fact, in a study of sustained load crack growth in a wide range of superalloys,[76] intergranular fracture was observed in the majority of alloys (IN625, X–750, IN800 and HS25) and was generally characterised by relatively sharp wedge shaped cracking induced by grain boundary sliding. The exception was PE16, in which the intergranular fracture was rough and indicated extensive cavity formation and growth.

Microstructure

Often a processing change, designed for example to modify grain size, is accompanied by other microstructural differences, so some caution is necessary in interpreting measured effects. It is also important to compare grain size effects in the same test regime, i.e. transgranular cycle dependent or intergranular time dependent. In general, however, it should be anticipated that changes in grain size, precipitate type and distribution, and distribution of alloying elements between the matrix and precipitates will effect time dependent cracking by modifying the environmental interactions and, possibly, by influencing the nature of deformation.

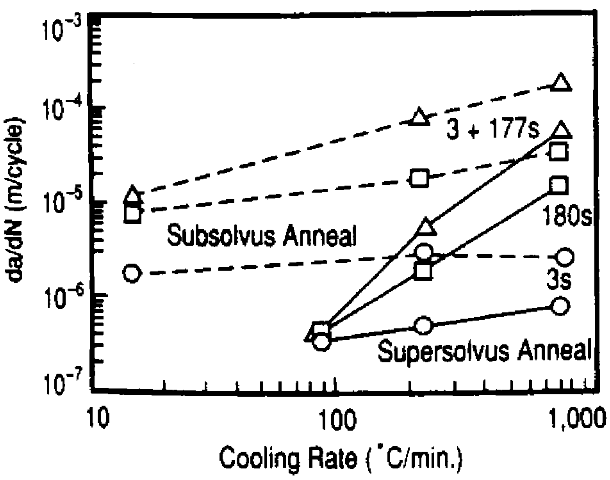
In general, fatigue crack growth rates in the time dependent regime in IN718 increase as the grain size decreases.[77–79] However, these studies showed that the lowest rates were obtained for a 'necklace' structure: large grains surrounded by necklaces of very small grains (Fig. 28). This is produced by warm or cold working followed by direct aging and partial recrystallisation.

It has been suggested that grain size per se is not the controlling factor, especially in alloys with a high volume fraction of precipitates (>35 vol.-%). In such cases the cooling rate from the solution temperature may play the predominant role in controlling crack propagation.[13] The effect of cooling rate on grain boundary precipitation is most pronounced for a coarse grain structure annealed at a supersolvus temperature. The effect of cooling rate from both below and above

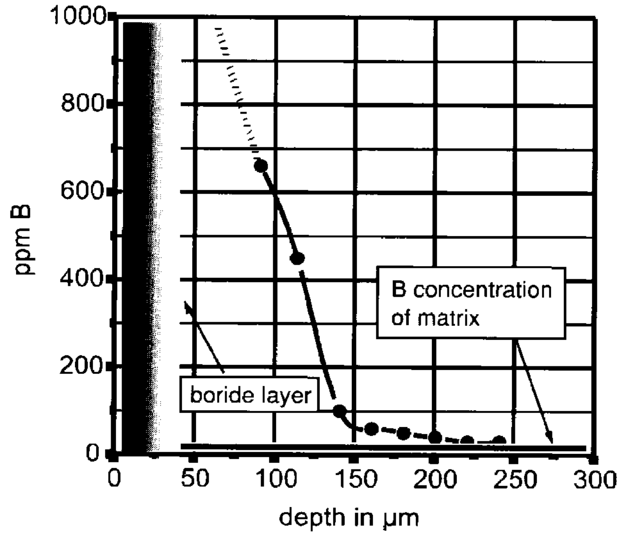


28 Effect of grain size on fatigue crack propagation behaviour at 538°C under hold time conditions: ASTM grain sizes: heat A=11·5, heat E=5, heat F=10·5, heat G (sheet)=10, heat G (forging with necklace)=5 (Ref. 77)

the gamma prime solvus temperature are shown in Fig. 29 for tests on powder metallurgy Rene 95. The cooling rate effect becomes more important with longer cycle periods. As shown in Fig. 29, a supersolvus anneal can fully suppress time dependence at 650°C with a hold time up to 177 s (still extremely short relative to service cycles) if the cooling rate is controlled below 100 K min^{-1}. Similar effects have been observed in Astroloy and IN100 (Ref. 80). The beneficial effect of slower cooling is believed to be a combination of local crack deflections along the serrated grain boundary interface and a local enrichment of chromium in the boundary regions.[13] For most alloys the lower cooling



29 Effect of cooling rate on fatigue crack growth rates in both subsolvus and supersolvus: solutioned P/M Rene 95 at 650°C with ΔK=30 MPa $m^{1/2}$ (Ref. 13)



30 Boron concentration profile of interdiffusion zone after heat treatment at 1000°C for 0·5 h (Ref. 81)

rate is accompanied by an increase in ductility but a decrease in strength and stress rupture life.

One aspect of intergranular cracking and embrittlement that has only recently been examined[24] has been the connection between the geometrical structure of grain boundaries and their propensity for cracking. The concept of coincident lattice sites (CLS) in which a Σ value indicates the period of atomic plane alignment at the boundary was used to examine time dependent fatigue cracking in alloy Rene88DT. A value of Σ1 indicates close alignment as in a low angle boundary. A value between 3 and 49 is considered a high angle CLS with high but decreasing coincidence. Grain boundaries with Σ values greater than 49 are considered random high angle boundaries (RHA), with low coincidence. It was found that low angle boundaries and Σ3 boundaries were highly resistant to intergranular cracking. However, of the high angle boundaries CSL boundaries appeared more susceptible than RHA boundaries. No specific data are available relating these observations to grain boundary diffusivity. However, these results clearly show how cracking tendency will vary according to the nature of individual grain boundaries.

Less has been published on IN706 than on IN718, but improvements in fatigue and sustained load cracking by microstructural control are possible. These alloys, with <35 vol.-% precipitate, may benefit from thermal–mechanical processing and specialised heat treatments. It has been reported that heat treatments that maximise the Ni_3Ti grain boundary phase can reduce the sustained load crack propagation by up to two orders of magnitude.[81] However, it is important to understand that compromises must be made for this alloy also. For example, to optimise the intermediate temperature tensile and creep properties, a heat treatment which developed Ni_3Nb/Ni_3Ti at the boundaries of a fine grain structure was recommended.[82] It should also be noted that by diffusing boron into ~150 µm of the surface, the intergranular cracking in this alloy was completely suppressed. The boron concentration profile after heat treatment is shown in Fig. 30 (Ref. 81). A 35 µm boride layer is at the surface and the enriched region contains borides in the matrix and grain boundaries.

There is, of course, a vast literature describing the effect of alloying additions and microstructural modifications on the tensile and creep strength of superalloys. The current understanding of the effect of alloy chemistry and microstructure on time dependent fatigue is far more limited although, as described above, some remarkable advances have been achieved. It should always be remembered that most laboratory tests are limited to a narrow range of cycle conditions in terms of time, temperature and stress. If any reasonable extrapolation to operating conditions is desired then it is essential to understand the fundamental processes involved. In this respect, there are two important and currently challenging obstacles to understanding: the grain boundary chemistry evolves by segregation of embrittling elements from the grain interior during exposure,[70,71] and the nature of the gas turbine environment may include elements that are more aggressive than oxygen[10] or that change the kinetics of oxygen penetration.[24]

Prevention and reversal of embrittlement

Gas phase embrittlement by some gases, such as hydrogen and chlorine, may be reversed simply by degassing at moderate temperatures if the species are still present in the elemental form. This may also be true for elemental sulphur embrittlement when exposed to dry hydrogen because the affinity of hydrogen for sulphur is greater than that of nickel for sulphur.[50] If there has been a chemical reaction, e.g. hydrogen reacting with carbon to form methane bubbles, or sulphur forming stable sulphides, reversal is unlikely. There is, however, the possibility that gas bubbles could be healed by hot isostatic pressing (hipping).

For oxygen embrittlement the author has more specific knowledge. If a stable chromium or aluminium oxide scale is formed, then the oxygen partial pressure is too low to produce intergranular oxygen embrittlement. This situation may be achieved by controlling the alloy chemistry or by applying a suitable coating. In addition to preventing oxygen ingress the authors have options to minimise intergranular penetration by adding boron,[39] or may modify the heat treatment to make the alloy more forgiving of embrittlement, generally by improving the intrinsic ductility.

Grain boundary migration, which is essential to alleviate the stress concentrations associated with grain boundary sliding, may be hindered by cavities or bubbles,[83] precipitates[84] or atoms in solid solution.[85] A series of experiments on various grades of nickel was designed to determine whether embrittlement owing to oxygen present in grain boundaries in various states could be reversed.[42] It was shown that dry hydrogen annealing could not reverse embrittlement resulting from pinning by gas bubbles, or by stable oxides of manganese, titanium, aluminium, zirconium or magnesium. However, nickel oxides were readily reduced by the hydrogen anneals. It was also demonstrated that, provided there were no stable oxide formers present, then a preanneal decarburisation in hydrogen prevented any subsequent oxygen embrittlement. Because commercial superalloys contain large amounts of stable oxide formers to produce the necessary strengthening phases and to confer the required oxidation and corrosion resistance, as well as added carbon, reversing oxygen embrittlement by hydrogen annealing is not possible. The observation of niobium oxide ahead of the crack tip in IN718 and similar alloys is one example of a stable oxide formed by oxygen penetration.[62]

These discussions in terms of preventing and reversing embrittlement refer to high temperature exposures and so called static embrittlement. For dynamic embrittlement, involving crack propagation in cyclic or sustained loading, the situation is somewhat different. As reported, there are indications that high chromium levels or boron additions can eliminate or reduce time dependent cracking. Preventing or minimising embrittlement is clearly important. However, reversing embrittlement ahead of a crack is not really an issue because penetration beyond a growing crack is expected to be on the order of a few atom spacings.[7] Repairing a cracked component then becomes a matter of removing all cracked material.

It might also be mentioned that sometimes a combination of static and dynamic embrittlement is involved. For example, in thermal fatigue cracking of a blade or vane section in a gas turbine the part is thermally cycled from a high temperature to a low temperature. Holding at the high temperature can lead to static embrittlement. Cooling to a low temperature leads to a maximum cyclic strain at an intermediate temperature where the alloy is most vulnerable to cracking.[86] It is also of interest to note that as the maximum temperature, or hold time at maximum temperature, is increased the crack growth rate first increases and then decreases. This is related to the minimum in isothermal fatigue life.[6]

Life prediction

For a number of years the principal challenge in high temperature design and analysis has been the prediction of component behaviour based on short term simple cycle fatigue testing. Many engineering approaches have been developed but none in common use recognise the specifics of environmental attack. Most, in fact, see time dependency of cracking as a creep related process. The exception is the frequency modified approach. Some of the more common approaches are briefly summarised below.

Linear life fraction

This approach considers the linear summation of the separated time independent and time dependent (creep) damage, and is given by

$$\sum \frac{N}{N_p} + \sum \frac{T}{T_p} = 1$$

where N/N_p is the cyclic part of the life fraction and T/T_p the time dependent part.

Frequency modified approach

This equation recognises that the environment is the principal time dependent factor but implies that cycle period alone is important.[87] The governing equation in its simplest form is

$$\left(N_f \nu^{k-1}\right)^{\beta} \Delta\varepsilon = F$$

where k, β and F are material constants. This was later modified to include hold time effects.

Hysteresis energy approach

A damage function that includes stress as well as strain range is used to describe failure.[88] The basic assumption of the method is that the net tensile hysteresis energy is a measure of damage and can be approximated by $\sigma_T \Delta\varepsilon_p$, where σ_T is the peak tensile stress. This energy term was then used in a similar manner to the frequency modified approach.

Strain range partitioning

It was proposed that the inelastic strain accumulated during one high temperature cycle could be partitioned into four possible kinds of strain range which depend on the direction of straining (tension or compression) and the type of inelastic strain accumulated (creep or time independent plasticity). Predicted lifetimes are calculated using the interactive damage rule

$$\frac{1}{N_{pred}} = \frac{F_{pp}}{N_{pp}} + \frac{F_{cp}}{N_{cp}} + \frac{F_{cc}}{N_{cc}} + \frac{F_{pc}}{N_{pc}}$$

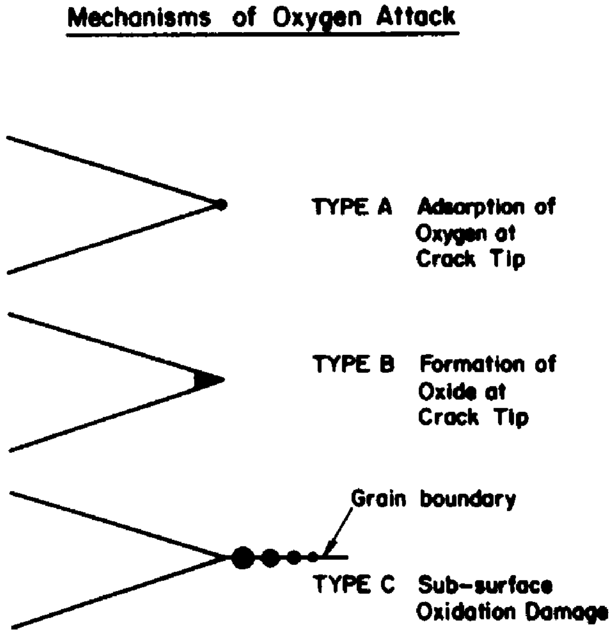
the types of strain ranges are identified as ε_{cp}, ε_{pc}, ε_{pp} and ε_{cc}, where, for example, ε_{pc} is that part of the inelastic strain range resulting from a plastic tension going strain balanced by a compression going creep strain.

Other approaches that have received some support are the damage rate approach,[89] crack propagation method[90] and damage parameter technique.[91] All these approaches can be criticised from both a functional and mechanistic perspective.

Oxygen interaction approaches

None of the approaches that have sought to incorporate what is known about the mechanism of crack tip oxygen attack have been developed to the point that definitive predictions and comparisons have been made. Before examining these approaches it is appropriate to review briefly what has been covered in this report and what needs to be incorporated in any comprehensive analysis scheme:

(i) time dependent intergranular crack propagation in air under either sustained or cyclic stress is a result principally of oxygen attack ahead of the crack tip
(ii) there is a strong effect of oxygen pressure with a relatively sharp transition between a maximum effect and a minimum effect
(iii) any separate effect of time dependent deformation (creep) is very small relative to the environmental effect
(iv) moisture can have a compounding influence beyond the effect of oxygen attack
(v) the ability to form a stable oxide scale can reduce or eliminate oxygen damage and time dependent cracking
(vi) certain elemental additions that segregate to grain boundaries can reduce the environmental damage
(vii) other elements besides oxygen can lead to intergranular failure and some are more aggressive at lower temperatures

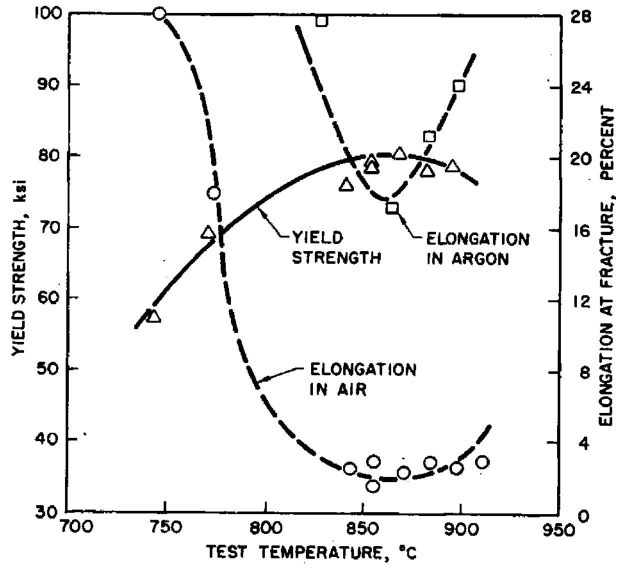


31 Crack tip damage mechanisms[26]

(viii) intergranular oxygen attack may occur at the tip of a propagating crack (dynamic embrittlement) or in the unstressed condition (static embrittlement)
(ix) the kinetics of oxygen penetration in the absence of moisture is predictable over the temperature range from about 1100 to 600°C
(x) intergranular cracking can be influenced by composition and microstructure (including the geometry of the grain boundary).

To re-examine the actual mechanism Fig. 31 is referred to. These three possible interactions have been reviewed comprehensively.[26] It was concluded that there is little to support a model of cracking occurring as oxygen atoms reach the crack tip (type A), and that crack tip oxidation is more likely to lead to crack blunting (type B). It was concluded that the available evidence (1983) pointed to oxygen penetration and intergranular oxidation reactions controlling time dependent crack propagation. The current review reaches the same conclusion based on the experimental evidence. Some authors, however, still invoke the atomic decohesion concept,[33] which may in fact be the dominant process for other elements such as sulphur, or the oxide cracking (SAGBO) mechanism.

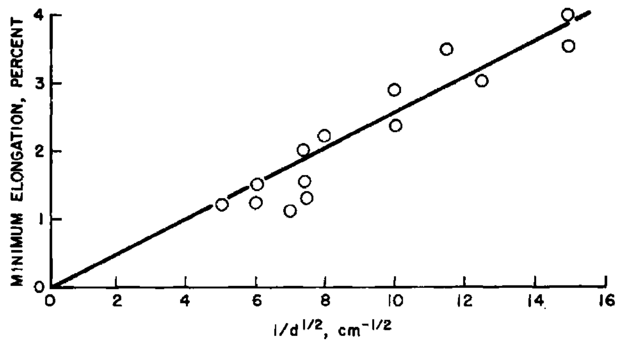
To unify the various ways in which intergranular oxidation reactions ahead of the growing crack can lead to time dependent cracking, a general qualitative theory incorporating grain boundary pinning that inhibits relief of local stress concentrations by boundary migration has been proposed. This process could occur over distances of just a few atom spacings in the limit. At very high temperatures and long periods relaxation of crack tip stresses by creep actually leads to an increase in fatigue life (decrease in crack propagation rate). This mechanism appears to be consistent with all reported observations. It can account for the effects of chemistry and microstructure and, in particular, accounts for the maximum in embrittlement (minimum in fatigue life) at an intermediate temperature. The small minimum in fatigue life in vacuum tests (compared with the much larger minimum in air tests) reported for IN706 (Ref. 6)



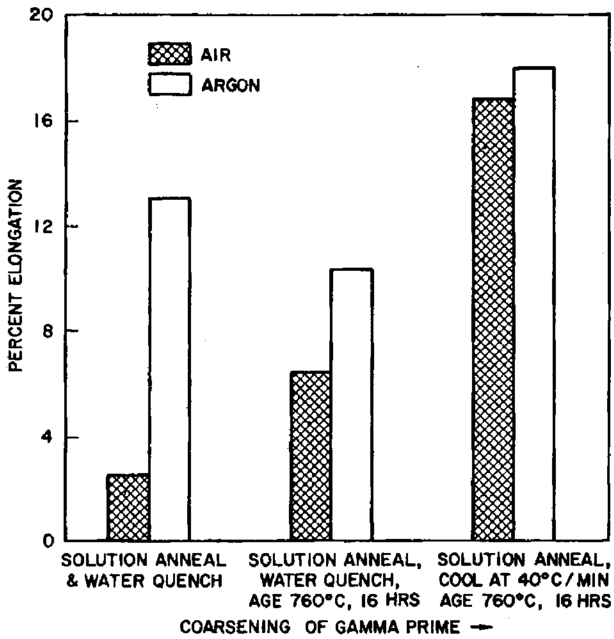
32 Variation with temperature of tensile ductility and yield strength in air and argon for Rene 41 (Ref. 92)

shown in Fig. 3 could be explained by the vacuum not being fully inert or an intrinsic ductility minimum. Because the vacuum was better than the minimum pressure normally required for inert behaviour it is more likely to be the latter. This would also explain the intergranular surface cracking observed at very low frequencies in high vacuum for A286.[14]

Some years ago it was shown for the alloy Rene 41 that there was a strong tensile ductility minimum in air tests at ~850°C compared with a much weaker minimum in argon.[92] This effect is shown in Fig. 32, in which the yield strength maximum coincides with the ductility minimum. This is a case of what the author has referred to as environmentally enhanced creep fracture, in which creep is broadly interpreted as time dependent deformation. It provides further support for the connection among the four main streams of investigation that the author has considered. The extent of the ductility minimum was found to be reduced with increasing grain size as shown in Fig. 33 for the solution annealed and water quenched condition, giving an ultrafine initial gamma prime precipitate. It was also shown that aging before testing to coarsen the precipitate and reduce the creep strength dramatically decreased the sensitivity to oxygen embrittlement and intergranular cracking. This effect is illustrated in



33 Minimum elongation at fracture versus reciprocal of square root of grain size for Rene 41 in solution annealed and water quenched condition[92]



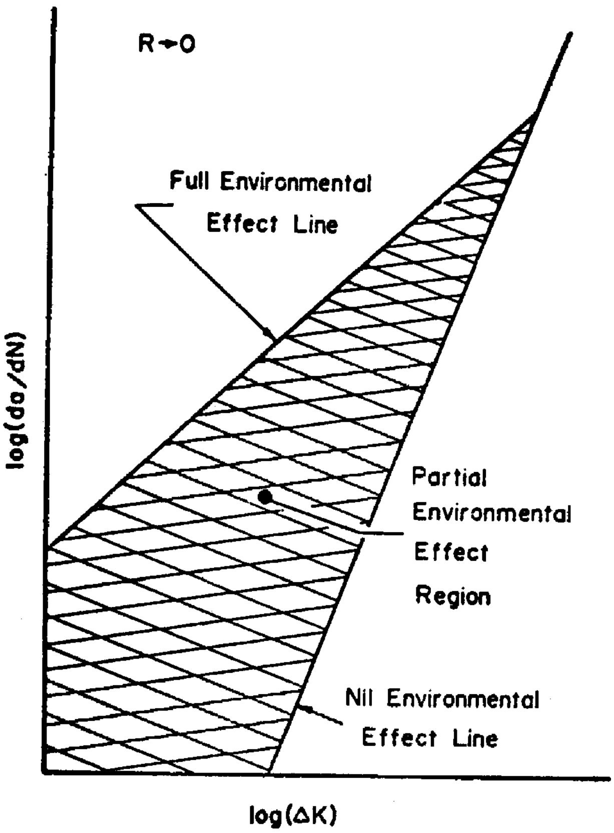
34 Comparison of minimum elongations in air and argon for three heat treatments in Rene 41 (Ref. 92)

Fig. 34. The water quenched specimens showed planar slip and evidence of intergranular cracking resulting from the stress concentrations. Slip was much more homogeneous after aging, especially in the slow cooled specimen so stress concentrations at grain boundaries were less likely to develop and, because of the lower creep strength, more likely to be relieved.

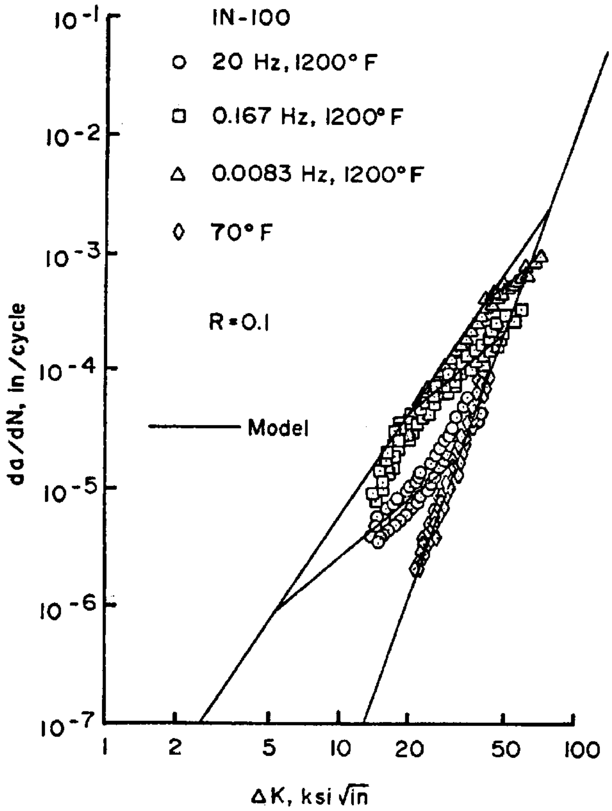
Ductility minima as well as fatigue life minima, whether a result of intrinsic embrittlement or induced by GPE, are expected to be sensitive to the test conditions as well as the microstructure and chemistry. Therefore, Fig. 3 for fatigue life minimum is a two dimensional section cut through number of cycles to fail *v.* temperature for a fixed frequency and Fig. 32 for ductility minimum is a similar cut in stress/temperature space at a fixed strain rate. Worst case situations in both types of tests would be expected to occur at lower temperatures for lower frequencies or strain rates.

None of the life analysis models have recognised the presence of a minimum in life and the idea that creep deformation is actually beneficial with increasing temperature. There is therefore no model capable of predicting the situation for very long term service situations. At this stage the author briefly examines some of the approaches that have shown promise over limited test ranges and which shed some light on the effect of the crack tip stress state on oxygen penetration.

To study the local interaction between the oxygen penetration process and the mechanical behaviour at the crack tip in IN718 a square wave oxygen pressure cycle, on either side of the transition pressure for time dependent cracking, was applied to both triangular and trapezoidal wave forms.[93] All tests were run at 650°C, with a load amplitude of 30 MPa $m^{1/2}$ and a load ratio of 0·3. Each position of the pressure cycle was held during 1 mm of propagation. Based on these experiments at the specific test conditions it was concluded that the damaging process is localised at the crack tip, insensitive to the K level during the loading part of the cycle, and it takes ~10 s after raising the pressure for



35 Kinetic model schematic[97]



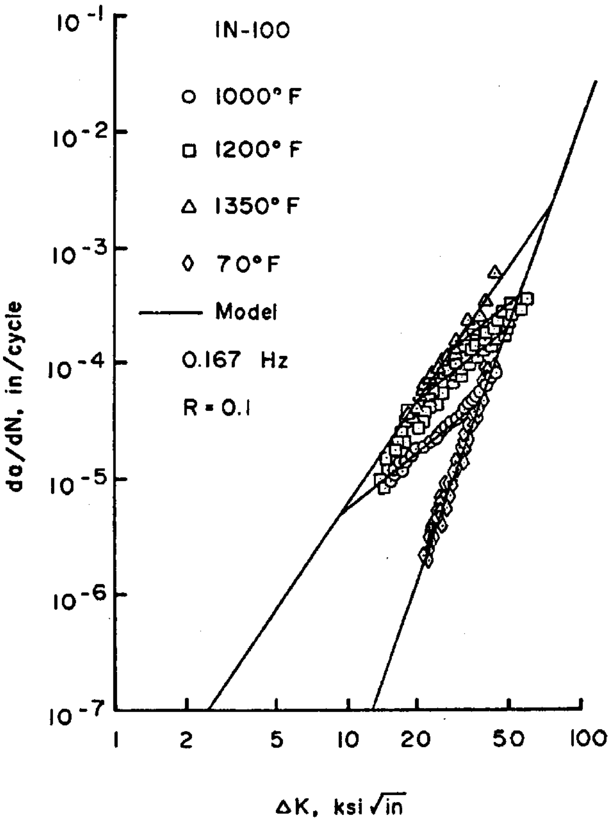
36 Frequency effect on fatigue crack growth in IN100 at 650°C (Ref. 97)

embrittlement to occur. The hold time study also showed that a microstructure with low creep strength and rapid relaxation should be more resistant to time dependent cracking.

Other studies have attempted to define an effective time t_{ox}, for the damaging effect of oxygen penetration to occur in the cycle. For example, it has been proposed to be half of the tensile part of the cycle,[94] or all the loading part.[95] An experimental attempt to measure t_{ox} concluded that, for the same frequency, varying the ratio of loading and unloading portions of the cycle did not influence the fatigue crack growth rate of IN718 at 650°C (Ref. 96). It was therefore concluded that, for this alloy under these conditions, the cycle effective oxidation time was equal to the total time of the cycle. Using this observation, and a derived relationship between K and the intergranular oxygen diffusion rate, estimates were made of crack growth rates for several test frequencies. Although the comparison is quite good, the range of test is limited and hold time tests were not included.

Direct measurements of intergranular diffusion rates as a function of stress ahead of a growing crack are extremely difficult because distances are so small and stress levels uncertain as the material creeps. Although it should be easier to study the effect of uniaxial stress on oxygen penetration using the methods described for unstressed penetration in nickel model materials,[10] to the author's knowledge, no such measurements have been reported. Life prediction methods must therefore depend on phenomenological approaches rather than analytical or theoretical methods.

One such model is shown schematically in Fig. 35. For a given material at a given ΔK level, there exists a corresponding fatigue crack increment per cycle Δa_f, which is caused solely by the fatigue process without environmental effects. For an effective cycle time period, Δt, the damaging species must move with the crack tip to be detrimental. During this time the intergranular penetration distance is Δa_p, which can be increased by increasing the temperature or reducing the frequency. If Δa_f is much greater than Δa_p , fatigue crack growth is caused primarily by the fatigue process alone. In this case, da/dN is frequency independent and is given by the limit line of no environmental effect as shown in Fig. 35. If Δa_p is greater than or equal to Δa_f, the environment has its full effect on da/dN. Any further increase in Δa_p by increasing the temperature or by reducing the frequency will not increase da/dN. This situation is therefore depicted by the limit line of full environmental effect as shown in Fig. 35. The crack growth mode changes from transgranular without environmental effects to fully intergranular with environmental effects. In the region between these two limits the rate controlling environmental effect becomes important and da/dN is temperature and frequency dependent. Using data on IN100 it was shown that, at a given temperature, the lines for different frequencies are parallel and, at a given frequency, the lines for different temperatures are parallel in this region. Some experimental results showing these effects are presented in Fig. 36 for different frequencies and Fig. 37 for different temperatures. The general applicability of the model appears very good. However, this model does not recognise the increased ability to relieve stress concentrations ahead of the crack tip at very long times or temperatures higher than that corresponding to a propagation rate maximum. Nevertheless the idea of



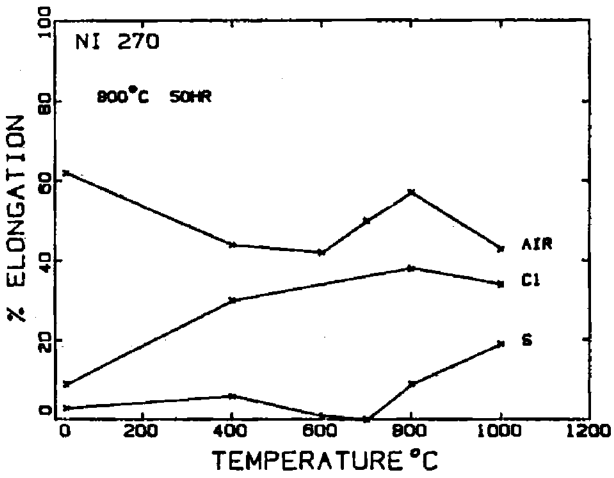
37 **Temperature effect on fatigue crack growth in IN100 (Ref. 97)**

both an upper bound on fatigue life (lower bound on crack propagation rate) similar to the data shown in Fig. 7, and a lower bound on life that is chemistry and microstructure sensitive, is attractive. The approach could serve as a framework to estimate the life of particular alloys operating in a specific temperature range.

Concluding remarks

It has been demonstrated that oxygen embrittlement (a specific example of GPE) is pervasive in nickel based alloys, and leads to both static (unstressed) and dynamic (ahead of a propagating crack) embrittlement. The mechanism has been discussed in some detail and the inadequacies of current engineering approaches to life prediction have been demonstrated. No experimental evidence supports significant stress acceleration of grain boundary oxygen diffusion. The kinetics of oxygen penetration for both static and dynamic embrittlement is similar, and is not affected appreciably by stress. This is consistent with there being little alteration of the interstitial boundary sites available for oxygen diffusion resulting from the application of a tensile stress.

Moisture, sulphur or chlorine might all lead to more rapid embrittlement and intergranular cracking at disc operating temperatures.[24,49,50] Figure 38 shows the effect of exposing Ni270 at 800°C in air, chlorine and sulphur on tensile ductility as a function of test temperature. Whereas there was no measurable oxygen embrittlement for this exposure, the entire specimen cross sections were embrittled and showed intergranular fracture at room temperature for chlorine and sulphur penetration.[49]

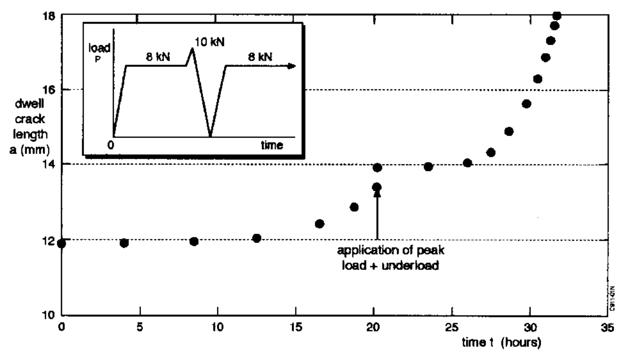


38 **Tensile elongation of Ni270 after 50 h exposure in air, Cl and S at 800°C**

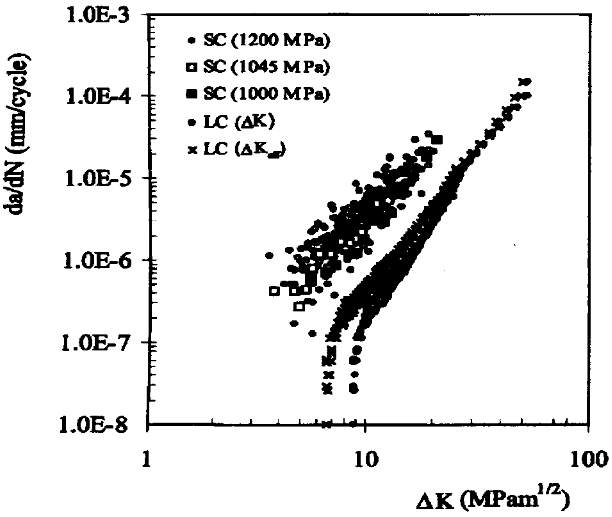
In a purely time dependent mode the total time at temperature for the disc provides a measure of the extent of intergranular embrittlement. The sustained load and any cyclic load are then perceived to be responsible for initiating and propagating a crack through the embrittled region. On this basis, and consistent with the idea of a best case (pure cycle dependent cracking) and a worst case (pure time dependent cracking), it should be possible to develop a testing method to pre-embrittle the grain boundaries before high frequency testing to accelerate a worst case assessment. Because the cycle dependent response is insensitive to chemistry and microstructure, the challenge is to develop the full environmental effect response for each alloy.

Whether or not the intergranular penetration of embrittling species leads to cracking will, of course, be determined by the operating thermal–mechanical conditions. A recent comprehensive study[98] of the comparison and interaction among sustained load crack propagation (referred to as dwell cracking), cyclic stress crack propagation, and simulated operating cycle crack initiation and propagation from a notch revealed many complexities. For example, a peak load and unload during sustained load cracking of IN718 at 600°C suppressed crack propagation as shown in Fig. 39. This was attributed to the formation of a compressive stress ahead of the crack tip.

Compressive stresses are frequently introduced into gas turbine discs by surface treatments such as shot peening. In addition to the induced surface residual



39 **Suppression of sustained load (dwell) cracking by peak load for IN718 at 600°C (Ref. 98)**



40 Small crack (SC) growth curves and long crack (LC) growth curves for Udimet 720 at room temperature[102]

stress, there are microstructural changes associated with cold work which may be the principal source of fatigue life improvement.[99,100] The surface roughness owing to dimple formation on impact can, on the other hand, create many potential crack initiation sites in the surface layer and therefore reduce the life. These conflicting contributions have been studied in terms of the process variables using designed experiments.[101] Although careful control of the variables can lead to significant improvements in short term fatigue life, the stability of these benefits at disc operating temperatures for the design lives has not been established.

In addition to the complexities associated with the detailed nature of the stress cycles and the local environment, there are some doubts as to the best formalism to describe cracking. The author has assumed that the elastic stress concentration factor is the appropriate correlating function, although there is evidence that this is not always the case.[17] Moreover, if it is a reasonable assumption for long cracks and small scale yielding at high temperatures, it may not apply for short cracks. Such cracks generally show faster crack growth rates, lower threshold levels and much greater scatter in rates than long through thickness cracks at equivalent ΔK levels.[102] An example is shown in Fig. 40 at room temperature for Udimet 720. Comparisons at elevated temperatures are not readily available although it is anticipated that similar differences would be observed.

Fatigue crack propagation (FCP) rate tests are usually conducted at a stress ratio close to zero ($R=K_{min}/K_{max}$) although, in service, loadings generally occur at nonzero stress ratios. The general trend noted in many studies is, on the basis of ΔK comparison, that FCP rates at a given temperature increase with increasing R. This complexity has not been factored into environmental interaction studies, although several empirical relationships have been proposed to correlate stress ratio effects.[17]

Finally, for gas turbine discs, in addition to the currently used shot peening described above, there are possibilities to reduce the amount of damage by modifying the surface chemistry using chromium based coatings or boron diffusion layers. However, it is unknown how such modifications will affect environmentally enhanced cracking caused by species other than oxygen. It is also possible to consider alternative heat treatments, possibly surface treatments, to lower the creep strength and therefore allow more stress relaxation to reduce the likelihood of crack initiation and inhibit crack propagation.

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