

OXYGEN ENHANCED CRACK GROWTH IN NICKEL-BASED SUPERALLOYS UNDER SUSTAINED AND FATIGUE LOADING

Robert P. Wei¹, Zhi-Fang Huang¹, Christopher Miller² and Gary W. Simmons²

¹Department of Mechanical Engineering and Mechanics

²Department of Chemistry

Lehigh University

Bethlehem, PA 18015

ABSTRACT

To better understand the role of niobium and other strengthening elements in the enhancement of crack growth by oxygen in nickel-based superalloys at high temperatures, three powder metallurgy (P/M) alloys, with nominal composition similar to alloy IN-100, but with 0, 2.5 and 5 wt pct niobium, were investigated. This investigation complements a previous study of an ingot metallurgy (I/M) Inconel 718. These P/M alloys are γ' strengthened (with comparable volume fractions of γ' precipitates of about 53 pct), and were designed to suppress the formation of γ'' precipitates. The alloys were tested in high-purity oxygen and argon under sustained and fatigue loading, at 873, 923 and 973 K. Companion microstructural and surface chemistry studies, including the oxidation of Nb, Ni₃Nb and NbC, were conducted to identify the mechanisms for crack growth enhancement. In this paper, the results from these investigations are briefly summarized. The mechanisms for crack growth and the role of niobium and other elements (Al, Cr, Fe, Ni and Ti) are discussed, and the relationship between sustained-load and fatigue crack growth is considered.

KEYWORDS

Nickel-based superalloys, oxygen enhanced crack growth, mechanisms, oxidation, microstructure, fracture mechanics, surface chemistry

INTRODUCTION

The influence of oxygen and moisture on crack growth in nickel-based superalloys at high temperatures has long been recognized. The presence of oxygen can increase the rate of crack growth under sustained loading by 4 orders of magnitude over that in inert environments. Considerable efforts have been made to understand the mechanisms for this enhancement, for example (1-7). Floreen and Raj (1) have categorized the various mechanisms into two groups. The first group involves environmentally enhanced formation and growth of cavities, or micro-cracks, at grain boundaries ahead of the crack tip. One such mechanism attributed the enhanced crack growth to the reaction of oxygen with grain boundary carbides to produce CO/CO₂ at high pressures (2). The second type is associated with preferential formation of a grain boundary oxide layer at the crack tip, either through the formation of oxides of nickel and iron (NiO and FeO) (3) or through a two-step process of forming first NiO and FeO and subsequently Cr₂O₃ (6).

Recent studies (8-11) on an Inconel 718 alloy (under sustained loading) and a Ni-18Cr-18Fe ternary alloy (in fatigue) suggested that niobium (Nb) can play a significant role, and raised concerns regarding the viability of these proposed mechanisms for crack growth enhancement by oxygen. The results showed that sustained load crack growth rates in oxygen at 973 K were increased, for example, by more than 10⁴X over those in high-purity argon for Inconel 718 (8). The enhancement in crack growth was attributed to the formation and rupture of a non-protective and brittle Nb₂O₅-type oxide film at the grain boundaries through the oxidation and decomposition of niobium-rich carbides and, perhaps, oxidation of γ'' precipitates at the grain boundaries. Crack growth rates in the ternary alloy, on the hand, were found to be essentially unaffected by

oxygen (11). A comparison of these results with those on a range of nickel-based superalloys in the literature showed the strong dependence of the environmental sensitivity factor (*i.e.*, the ratio of crack growth rates in the deleterious and inert environments) on Nb concentration (8). The sensitivity factor increased by up to 10^4 X for Nb from 0 to 5 wt. pct, *albeit* the sensitivity varied widely among the alloys. These findings suggested that the role of Nb on enhancing crack growth in oxygen, heretofore not recognized, needs to be carefully examined. The “insensitivity” of the Ni-18Cr-18Fe ternary alloy, with copious amounts of $M_{23}C_6$ carbides at the grain boundaries, calls into question the viability of both groups of proposed mechanisms.

In this paper, the results from a series of coordinated crack growth, microstructure and surface chemistry studies to elucidate the role of niobium on crack growth in oxygen at high temperatures are summarized (12-16). These studies complement the earlier work on Inconel 718 at Lehigh University (8). Three γ' -strengthened powder metallurgy (P/M) alloys, with nominal composition similar to alloy IN-100, but with 0, 2.5 and 5 wt. pct. niobium, were investigated. The chemical compositions of these alloys (in wt pct) are as follows: Alloy 1 (Ni56.3 Cr12.7 Co18.9 Al4.8 Ti3.9 Mo3.3 Nb0); Alloy 2 (Ni56.4 Cr12.1 Co18.3 Al4.1 Ti3.3 Mo3.2 Nb2.5); and Alloy 3 (Ni54.5 Cr12.3 Co18.2 Al3.7 Ti3.3 Mo3.3 Nb4.9). These alloys were designed to suppress the formation of γ'' (and δ) precipitates. They have comparable volume fractions of γ' precipitates of about 53 pct. The hardness and average grain size for alloys 1, 2 and 3 were about Rockwell C 45, 45 and 47, and 10, 45 and 45 μ m, respectively. The average size of the γ' precipitates within the γ matrix for all three alloys is approximately 150 nm, except for the presence of about 3 vol. pct of micrometer sized coarse γ' precipitates in alloy 1. Surface chemistry studies were also carried out on Nb, Ni_3Nb and NbC to assess the reactivity of these phases to oxygen. Based on the findings and information in the literature, the mechanisms for crack growth and the role of niobium and of other elements are considered.

SUMMARY OF RESULTS

Crack Growth and Corollary Experiments

Sustained-load and fatigue crack growth experiments were conducted on the P/M alloys in the circumferential-radial (CR) orientation in high-purity oxygen at 873, 923 and 973 K (12,16). Because of the very slow rates of growth, testing in high-purity argon was limited to the intermediate K levels at 973 K for the alloys. The data, showing crack growth rates under sustained-load versus K, are presented in Fig. 1 as a function of temperature for alloys 1 and 3. The results show that the crack growth rates in oxygen at 135 kPa are strongly dependent on temperature, with apparent activation energy of about 250 kJ/mol. The rates and crack growth response in the Nb-containing alloy 3 parallel those of Inconel 718 and the growth rates were about 10^4 X faster than those in argon ($p_{O_2} < 10^{-17}$ Pa) (see Fig. 1a). Results on the niobium-free alloy 1 were somewhat surprising in that the growth rates in oxygen were nearly 10^3 X faster than those in argon at 973 K (see Fig. 1b); *i.e.*, with an environmental sensitivity that is well above the anticipated 1X to 10X. Data on alloy 2 were comparable to those of alloy 3 (12).

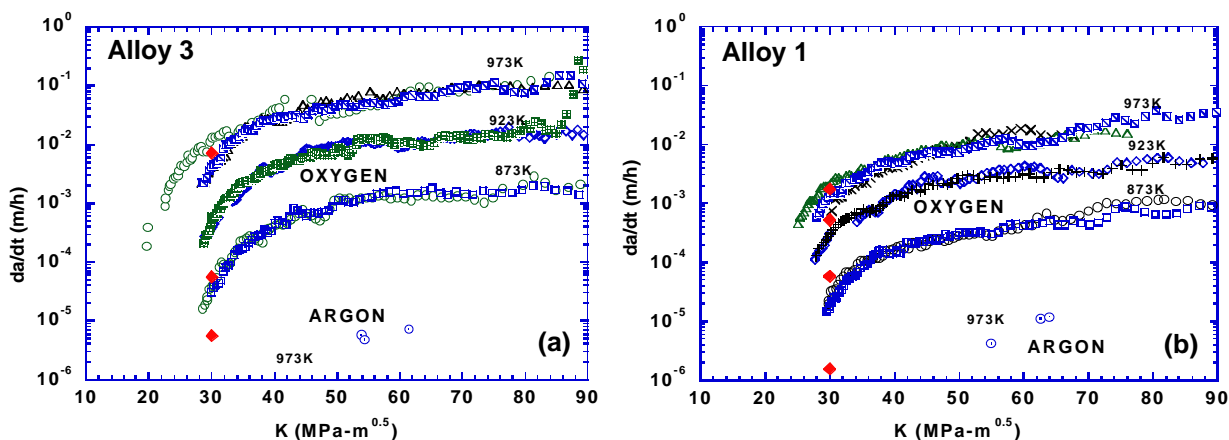


Figure 1: Kinetics of sustained-load crack growth (a) in the Nb-containing alloy 3 and (b) the Nb-free alloy 1 in high-purity oxygen and argon, and comparisons with crack growth rates inferred from the dwell-time fatigue tests (12,16).

Fatigue crack growth experiments were conducted as a function of dwell-time at peak load (from 0 to 30 s), using a trapezoidal waveform. The rise and fall time, at 0 s dwell-time, corresponds to a triangular-wave loading at 10 Hz. Representative data (for alloy 3 in oxygen) are shown in Fig. 2. Because of the strong sensitivity to oxygen enhanced growth, the fatigue crack growth rates were essentially dictated by the

growth during the dwell-time at load, and hence the sustained-load crack growth rate. This is reflected by the sustained-load crack growth rates that were back calculated from the fatigue data in Fig. 1 (12,16).

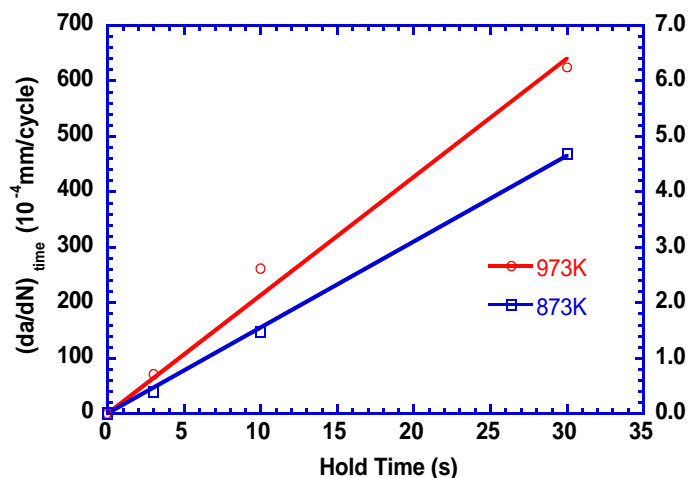


Figure 2: Effect of dwell-time on the time-dependent component of fatigue crack growth rate, $(da/dN)_{time}$, for alloy 3 in oxygen at $DK = 27 \text{ MPa}\cdot\text{m}^{1/2}$ (12,16).

Representative microfractographs of the niobium-free alloy 1 and niobium-containing alloy 3 tested in high-purity oxygen, under sustained load, at 973 K are shown in Fig. 3 (12,17). Cracking in alloy 1 was essentially intergranular and also followed along interfaces between the large (micrometer sized) γ' precipitates and the matrix, some of which are indicated by the arrows in Fig. 3a. For alloy 3, cracking was predominately intergranular. Many small particles (appearing in white) are seen on the grain boundary surfaces, and were found through energy dispersive spectroscopic (EDS) analyses to be rich in Nb. These particles are consistent with the Nb-rich carbides found previously on the grain boundaries of Inconel 718 (18). The fracture surface morphology for the alloys tested in fatigue paralleled that of sustained loading, and indicated that the micromechanisms for oxygen enhanced crack growth were identical (12,16,17).

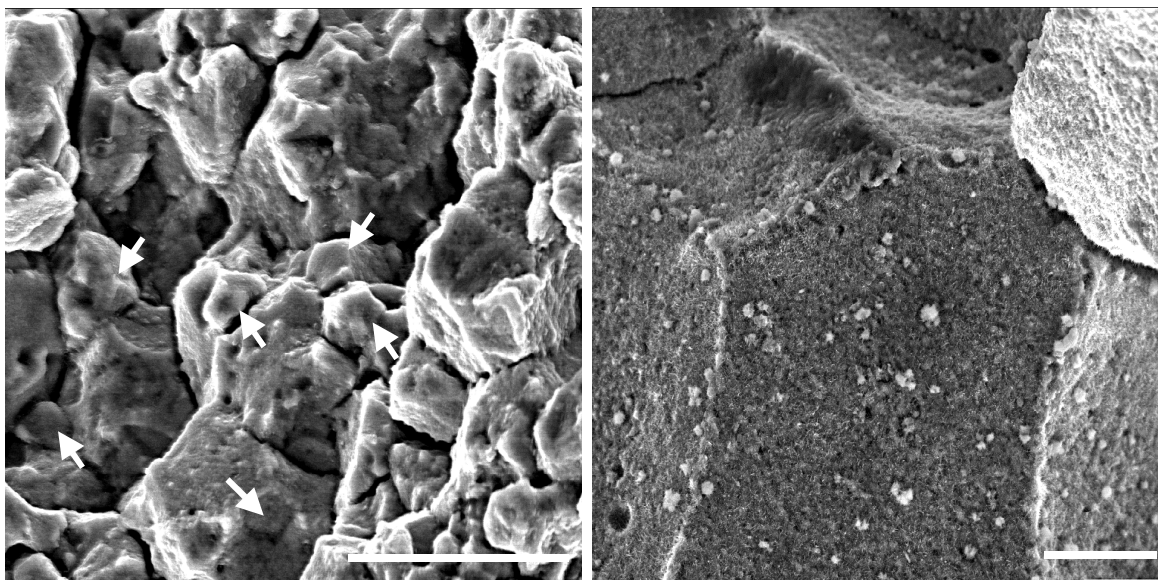


Figure 3: Microfractographs of (a) the Nb-free alloy 1 and (b) the Nb-containing alloy 3 tested in oxygen at 973 K (12,17).

Surface Chemistry Studies

To determine the reactivity of the alloys to oxygen, polished and ion-sputtered surfaces of alloys 1 and 3, as well as Inconel 718, were analyzed by X-ray photoelectron spectroscopy (XPS) in vacuum at 10^{-7} Pa, and following exposure to 5×10^{-4} Pa of oxygen at 873, 923 and 973 K for 2,700 s (14,15). The results suggest that preferential oxidization occurred, even at 10^{-7} Pa, for Al, Cr, Nb and Ti in alloy 3, and for Cr and Nb in Inconel 718.

To provide direct evidence for the reactions of Nb compounds with oxygen, specimens of Nb, Ni_3Nb (with γ'' crystal structure) and a specially grown film of NbC were given the same exposure to oxygen at 873, 923

and 973 K and analyzed by XPS (13). Representative spectra for Ni₃Nb and the NbC film at 973 K are shown in Fig. 4 along with the component spectra for Ni₃Nb and NbC and the various oxides that were formed. The results confirm the fact that both Ni₃Nb and NbC react with oxygen at these temperatures to form niobium oxides of ranging stoichiometry, with a greater propensity for Ni₃Nb to oxidize to Nb₂O₅.

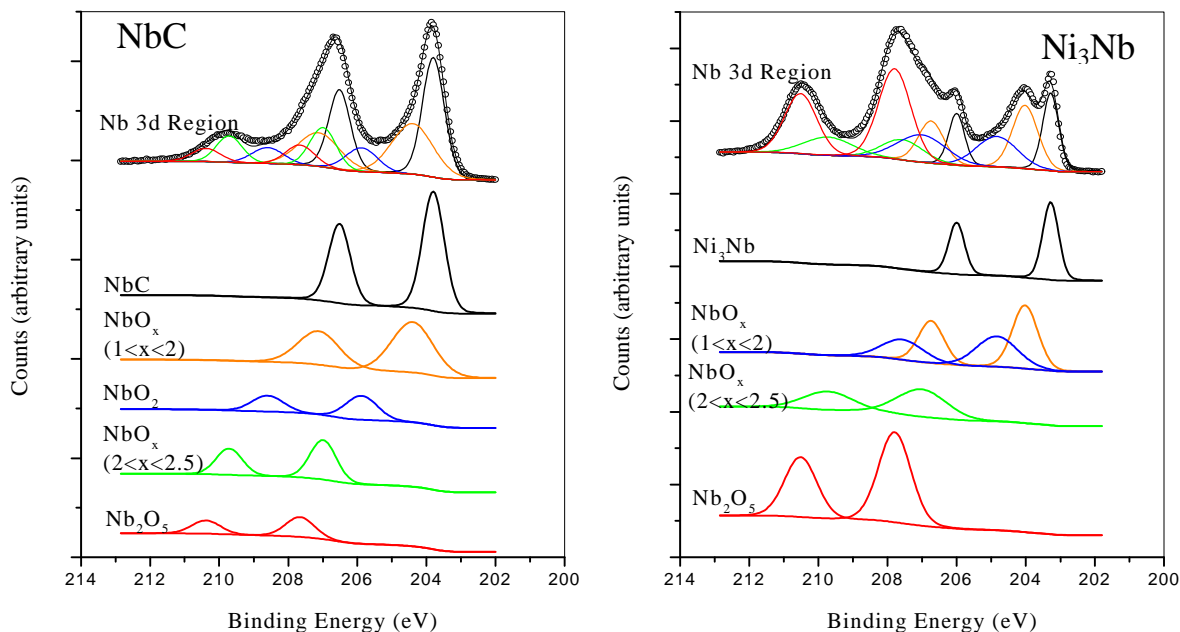


Figure 4: XPS spectra (Nb region: 3d_{3/2,5/2}) of NbC and Ni₃Nb after oxidation at 973 K in 5 x 10⁻⁴ Pa of O₂ for 45 minutes (13).

Oxidation Ahead of the Crack Tip

To ascertain the existence of an “oxygen embrittled” zone ahead of the tip of a growing crack, interrupted experiments were carried out whereby sustained-load crack growth in oxygen was stopped. The specimen was partially unloaded and the test chamber was evacuated and back-filled with ultrahigh purity argon, and was then reloaded to the same test load. Representative crack growth response for a specimen of alloy 3 tested at K = 33 MPa·m^{1/2} and 873 K is shown in Fig. 5 (12). The results showed the presence of an embrittled zone of about 80 μm over which the crack growth rate decreased from the pre-interruption rate in oxygen to that for argon. The profile is qualitatively consistent with that of the concentration profile associated with oxygen diffusion.

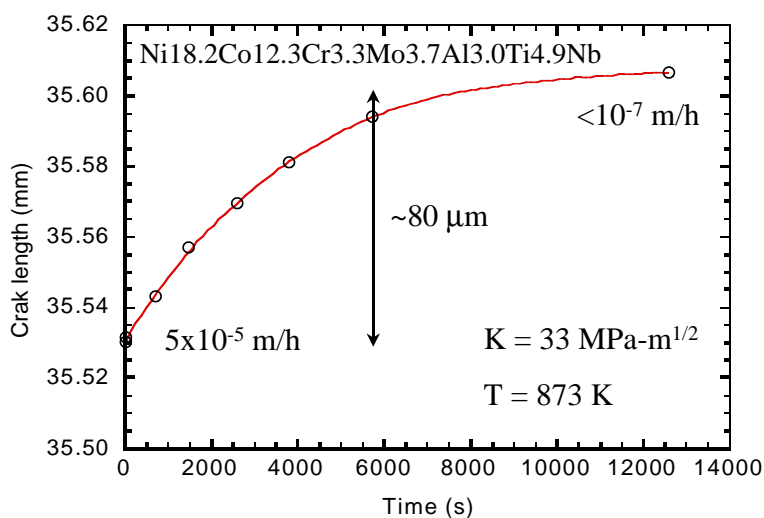


Figure 5: Representative crack growth response for a P/M alloy in ultrahigh purity argon following prior growth in oxygen (12).

To determine which elements might be oxidized ahead of the crack tip, samples containing the crack tip region (at K = 60 MPa·m^{1/2}) were cut from interrupted test specimens. They were electrolytically charged with hydrogen, and broken under ultrahigh vacuum and analyzed by XPS. Normalized oxidation profiles across the crack tip, for Inconel 718 and alloy 3, tested in oxygen at 973 K, are shown in Fig. 6. It is clear

that Nb and Cr oxidized ahead of the crack tip in Inconel 718 to an estimated distance of 150 μm , with Nb as the more active element. The finding was the same for alloy 3, except that the extent of reaction was less and the indicated depth of penetration was only about 100 μm . The difference between Inconel 718 and alloy 3 is attributed to the much higher concentration of Al and Ti in alloy 3, which would oxidize ahead of Nb and Cr. Because of instrumental limitations, information on Al and Ti could not be quantified; but oxidation ahead of the crack tip in alloy 3 is expected to extend out to 150 μm as well. Equally significant is the fact that there was no evidence for Fe and Ni oxidation ahead of the crack tip.

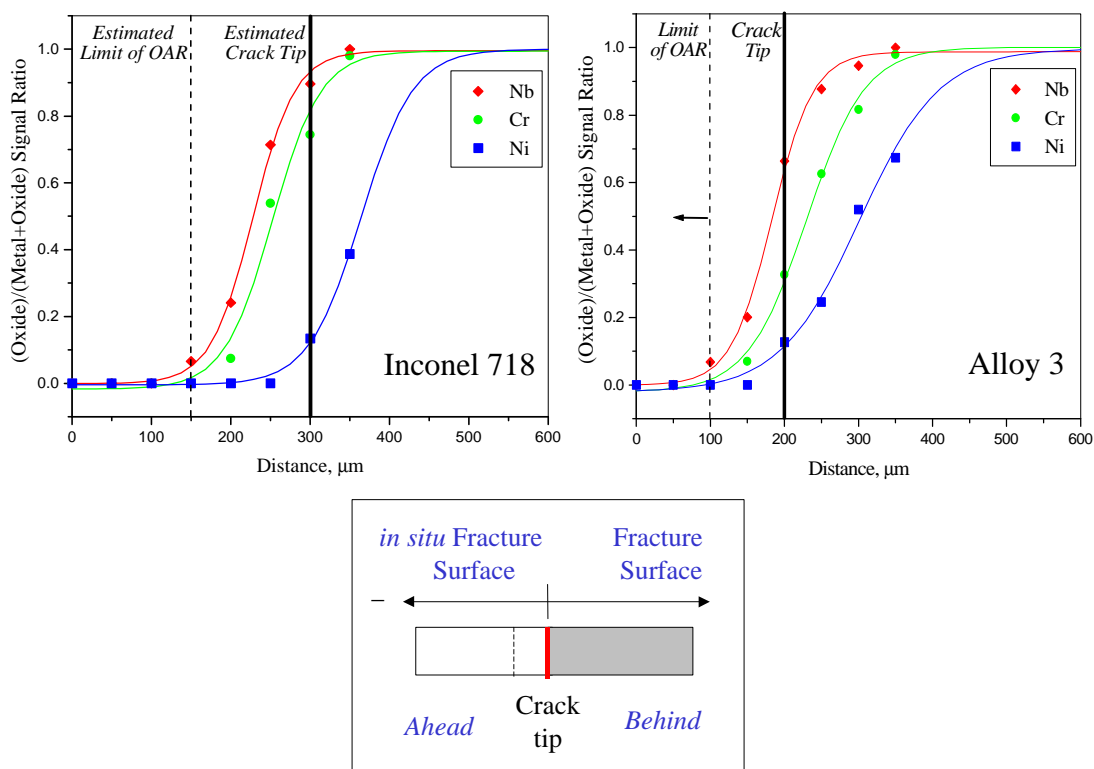


Figure 6. Normalized oxidation profile showing the oxide formation for Nb, Cr, and Ni on Inconel 718 fracture surfaces vs. distance (μm), and the estimated boundaries of the oxygen affected region (OAR).

MECHANISMS FOR OXYGEN ENHANCED CRACK GROWTH

These results confirmed the postulated role of niobium in enhancing the rate of crack growth in oxygen at high temperatures. The enhancement mechanism is the oxidation and decomposition of niobium rich carbides at the grain boundaries to form a brittle film of Nb_2O_5 -type oxides on the boundary surfaces. The fact that these alloys were designed to suppress the formation of γ'' - Ni_3Nb precipitates reinforces the role of niobium rich carbides as a source of Nb for embrittlement. The XPS results on the reactions of oxygen with Ni_3Nb , however, showed that Nb was preferentially oxidized over Ni, and that the reactions were more rapid than those with NbC. The Ni_3Nb precipitates, therefore, also play a significant role in the enhancement of crack growth in the γ'' strengthened alloys, such as Inconel 718. In the absence of Nb (*e.g.*, alloy 1), the oxidation of Al and Ti appears to be the cause for enhanced crack growth, and the site of “embrittlement has been identified with the γ - γ' interfaces. The fact that results indicate that Ni and Fe do not oxidize ahead of the crack tip suggests that the mechanisms involving the oxidation of these elements may not be viable. Although Cr oxidizes, the absence of environmental sensitivity in the Ni-Cr-Fe ternary alloy suggests that it is also not a player. The observed environmental sensitivity, particularly to Nb, indicates that the embrittlement process involved oxidation, and suggests that oxygen adsorption *per se* is not a viable mechanism. The results were integrated and compared with available data on other superalloys. The role and contribution of the various phases were interpreted with the aid of a superposition model for crack growth (18); namely, between the niobium-rich carbides and the γ'' precipitates in Inconel 718, and between these carbides and γ' precipitates in the P/M alloys (alloys 1, 2 and 3).

SUMMARY

As a part of a study to elucidate the role of niobium on crack growth in oxygen at high temperatures, crack growth experiments and microstructural analyses were carried out on three γ strengthened powder metallurgy (P/M) alloys, with 0, 2.5 and 5 wt. pct. niobium. Companion surface chemistry studies of the oxidation of Nb, Ni_3Nb and NbC were also conducted. The results were integrated and compared with available data on other superalloys, and were interpreted with the aid of a superposition model for crack growth. The results indicate that niobium contributed significantly to the enhancement of crack growth by oxygen in both γ' and γ'' strengthened alloys. They support the previous suggested mechanism of oxidation and decomposition of Nb-rich carbides at the grain boundaries. For the Nb-free, γ' strengthened alloys, crack growth enhancement is attributed to the oxidation of Al and Ti (*versus* Cr, Fe and Ni) and is correlated with the volume fractions of fine and coarse γ' precipitates.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support of this research by the Division of Materials Research of the National Science Foundation, under Grant DMR-9632994, and the technical assistance and insightful discussions by Paul Reynolds of Pratt Whitney on the metallurgy of nickel-based superalloys, and by Alfred Miller of Lehigh University on x-ray photoelectron spectroscopy. CM also wishes to acknowledge the support of a NSF IGERT Traineeship during academic year 2000-01 under Grant DGE-9987548.

REFERENCES

1. Floreen, S. and Raj, R. (1984). In: *Flow and Fracture at Elevated Temperatures*, pp. 383-405, Raj, R. (Ed.). Am. Soc. Metals, Metals Park, OH.
2. Woodford, D.A. and Bricknell, R.H. (1982) *Acta Met.* 30, 257.
3. Gabrielli, F. and Pelloux, R.M. (1982) *Met. Trans. A* 13A, 1083.
4. Bain, K.R. and Pelloux, R.M. (1984). In *Proc. of Conf. on Superalloys*, pp. 387-396. The Metall. Soc./AIME, Warrendale, PA.
5. Bain, K.R. and Pelloux, R.M. (1984) *Met. Trans. A* 15A, 381.
6. Andrieu, E., Ghonem, H. and Pineau, A. (1991). *Elevated Temperature Crack Growth*, (Paper presented at the ASME Winter Annual Meeting, 25-30 November, 1990, Dallas, TX 1991), 25.
7. Lynch, S.P., et al. (1994) *Fatigue Fract. Engr. Mater. Struct.* 17, 297.
8. Gao, M., Dwyer, D.J. and Wei, R.P. (1995) In: *Superalloys 718, 625, 706 and Various Derivatives*, pp. 581-592 E.A. Loria, (Ed.). The Minerals, Metals & Materials Society, Warrendale, PA.
9. Gao, M., Dwyer, D.J. and Wei, R.P. (1995) *Scripta Met. et Mater.* 32, 1169.
10. Dwyer, D.J., Gao M. and Wei, R.P. (1994), *Applied Surface Sci.* 81, 229.
11. Chen, S.F. and Wei, R.P. (1998) *Mats Sci. & Engr.* A256, 197.
12. Huang, Z.F., (2001) Ph.D. Dissertation, Lehigh University, Bethlehem, PA.
13. Miller, C.F., Simmons, G.W. and Wei, R.P. (2000) *Scripta Mater.* 42, 227.
14. Miller, C.F., Simmons, G.W. and Wei, R.P. (2001), *Scripta Mater.* 44, 2405.
15. Miller, C.F., (2001) Ph.D. Dissertation, Lehigh University Bethlehem, PA.
16. Wei, R.P. and Huang, Z.F. "Influence of Dwell-Time on Fatigue Crack Growth in Nickel-Base Superalloys", submitted to *Materials Sci. & Engr.*
17. Wei, R.P. (2000). In: *Advanced Technologies for Superalloy Affordability*, pp. 103-112 K.M. Chang, S.K. Srivastava, D.U. Furrer and K.R. Bain (Eds.). The Minerals, Metals & Materials Society, Warrendale, PA.
18. Gao, M. and Wei, R.P. (November 1997) *Scripta Mater.* 37(12), 1843.