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MICROSTRUCTURAL DEPENDENCE OF CAVITATION DAMAGE IN POLYCRYSTALLINE MATERIALS

Final Report

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NOTICE

Introduction

Intergranular stress corrosion cracking (ISCC) refers to cracking that propagates along the grain boundaries of polycrystalline materials under the combination of applied stress and a corrosive environment. That the vulnerability of individual grain boundaries to ISCC would be affected by local grain-boundary structure has long been suspected, but only recently have observations of local structure been systematically correlated with damage. These observations focus mainly on lattice misorientation as a convenient classification of the structure of grain boundaries. Lattice misorientation constitutes a three-dimensional projection (hypersurface) through the much larger fundamental zone reckoning the five macroscopic degrees-of-freedom (homogeneous space) of physically distinctive structural types.

Within the context of this projection, recent studies have concluded that general high angle grain boundaries are much more vulnerable to ISCC damage than low-angle and special high-angle boundaries in some nickel-based alloys. The intergranular corrosion susceptibility of grain boundaries in high-purity (polycrystalline) nickel was studied by Palumbo and Aust [1] in a corrosive environment consisting of $2NH_2SO_4$ at 303° K. Their central observation is that low-angle grain boundaries, and vicinal boundaries with lattice disorientations near low-Σ coincidence site lattices (CSLs), are found to be more resistant to localized corrosion than other high-angle general boundaries. Crawford and Was [2] assessed the vulnerability of grain boundaries in Inconel Alloy 600 to ISCC damage in argon and high-purity water at 633° K. Using a classification similar to that of Palumbo and Aust, they separated observed grain boundaries into three groups: (i) low-angle boundaries, (ii) CSL boundaries, and (iii) general (random) high-angle boundaries. Using selected area channeling patterns to orient the lattice, they found that low-angle boundaries are rarely damaged, and that CSL boundaries are only half as susceptible to ISCC as compared with general high-angle boundaries.

Although the classification set selected in these pioneering studies is rather coarse, and does not explicitly incorporate information about boundary plane orientation and connectivity, the results nevertheless suggest a tendency for small-angle and low-Σ boundaries to be resistant to ISCC damage under certain environmental conditions. It follows that the distribution and connectivity of grain boundary types could potentially affect the overall ISCC performance of these materials. Since it is also known that the distribution of grain boundary types can be substantially altered by processing variations [3], it is useful to consider the engineered alteration of grain-boundary structure as a potential vehicle for improving ISCC performance in nickel-based alloys.

The purpose of this two-year study has been to take a somewhat broader view of the problem, which includes the dependence of ISCC on boundary inclination. More precisely, the aim was to investigate the role of grain-boundary structure in ISCC damage, with particular attention to crack propagation and the relationship of grain-boundary normal orientation (relative to the direction of maximum tensile stress), in addition to grain-boundary geometry. This was accomplished by refining the classification set to explicitly include the boundary normal orientation as a variable. Also, we wanted to extend the previous work to another alloy system; the material selected was Inconel alloy X750. The new method of orientation imaging microscopy (OIM) [4] has been used to rapidly determine the crystallographic character of grain boundaries; this has been coupled with precision serial sectioning to reveal the full five parameters of structure for each exposed boundary. An important advantage is that many grain boundaries can be examined in a realistic time frame, and that the full (mesoscopic) structure can be accessed from the experiments.

Experimental Methods

The sample studied is a standard compact tension test specimen. ISCC was developed on the basis of a pre-existing notch which was subsequently fatigue precracked before exposure to the corrosive environment. The corrosion test was performed under a constant displacement condition, using a bolt to induce opening of the notch (wedge opening loading). The initial stress intensity factor was 49.4 $MPam^{-1/2}$, corresponding to a tensile stress of 30% of yield. The stress intensity decreases as the crack propagates through the material. The test environment consisted of high temperature (633°K) deaerated water. The pH of the solution was 10. No electrochemical potential was applied to the sample. The average crack growth rate fell in the range of 2.69-3.42 $x10^{-10}$ m/s.

OIM was used to reveal the microstructure adjacent to the crack path. In order to reveal the three-dimensional geometry of the grain-boundary network, which is obscured by the opacity of the material under optical or scanning electron-optical examination, a serial sectioning procedure was adopted. The approach is straightforward; the sample is polished down perpendicular to the observation surface by a measureable amount. Vickers microhardness indents were introduced into the surface at strategic locations. Upon polishing, the reduced exposed area of these indents is measured. From the known angles of the indenter it is then possible to estimate the thickness of the removed layer. In total, ten layers of material were exposed. Each of the three strata were fully characterized using OIM; approximately 90,000 single orientation measurements were obtained from each layer as the basis for the OIMs. The step size between measurement points was selected to be 10 µm; scanning occurred over hexagonal grids. The ten sections were separated into three groups to insure that different grains were exposed in three separate strata. At least four microhardness indentations were employed on each section to facilitate the estimates of removal thickness. Based upon an analysis of possible errors, the limiting resolution of grain boundary inclination angle is believed to be ~9°.

Materials Characterization

The sample analyzed is of Inconel Alloy X750. The chromium content is 15.5%, which is about the same level found in Alloy 600 (16%). The sample was rolled at high temperature, solution annealed at 1366 °K for one hour, and then age-hardened at 977 °K for 20 hours. From standard optical metallography the measured average grain size of the material is 114 µm, but the more sensitive OIM revealed the average grain size to be 89 µm. The material exhibits a Knoop hardness of 350 using a 200 gram force. Measured yield stresses are 744 MPa at 294 °K and 689 MPa at 633 °K, which is the temperature at which corrosion testing was performed. Young's modulus for this material is 207 GPa at 294 °K, and Poisson's ratio is 0.29.

Alloy X750 is a precipitation hardened material; the main hardening agent is the intermetallic γ' phase ($Ni_3(Al,Ti)$). In addition, a prominent feature of the microstructure is the carbide precipitation (M_7C_3 and $M_{23}C_6$) on (primarily) the grain boundaries. In the sample of interest 60-70% of the grain boundaries are observed to contain carbide precipitates.

The orientation and misorientation textures of the sample were both obtained using OIM. The misorientation distribution function (MODF) is substantially impacted by the formation of twins during annealing. A maximum intensity of 7.8 times-random is found centered upon the Σ-3 misorientation. A secondary peak can be identified at the location of the Σ-9 misorientation. This misorientation distribution of the material was examined in the narrower context of the CSL theory. The total set of 31,612 measured grain boundaries were classified into small angle boundries (Σ1), Σ3 boundaries (presumably twins), other low-Σ special boundaries (Σ5, ..., Σ49), and all other random high-angle boundaries (HABs).

Primary Results of the Research

Sensitivity of Crack Propagation to the Microstructure: Altogether, 818 triple junctions in the measurement set were exposed to the advancing crack. It is useful to consider the decisions the advancing crack tip makes as it propagates on either one leg or the other of each triple junction. Of the 818 triple junctions encountered, 541 junctions included a grain boundary with Σ3 character. *In no case was a Σ3 boundary found to crack.* Thus, whenever one branch of a triple junction exhibited Σ3 misorientation the crack followed the other branch or was arrested. (Several instances were observed where the crack was arrested at a triple junction, re-emerging one-grain further along the forward direction of propagation. These arrests were always associated with triple junctions containing one Σ3 boundary, and another boundary unfavorably oriented for crack propagation.) Of the remaining 277 triple junctions, only two low-angle (Σ1) boundaries were found to be cracked. Upon closer examination of these two boundaries it was found that one had disorientation of 14.5° and the other 14.6°. Thus, both fell near the limit of what is normally considered to be small angle. We have concluded that *low-angle grain boundaries are very resistant to intergranular cracking in this material.* Among the total set of observed triple junctions encountered by the advancing crack, 42 cracked boundaries fell in the low-Σ category (Σ1-Σ49) according to Brandon's criterion. It is interesting that when the more restrictive Palumbo-Aust criterion [1] is applied, only three of these boundaries are conserved in the low-Σ class. Thus, it would appear that when a suitably restrictive criterion is used, *the evidence suggests that low-Σ boundaries are more resistant to intergranular cracking.*

Although the possible errors in resolving boundary normal orientation are estimated to be quite large (~9°), we have nevertheless considered crystal plane orientations at cracked and uncracked boundaries. With respect to Σ3-misoriented boundaries, we find only moderate clustering of these to be associated with the (111) coherent plane of the symmetrical twin boundary. The fact that not even a single Σ3 boundary was found to be cracked suggests that crystal plane orientation may not play a significant role for this class of boundaries. In the broader context, *when the entire population of 818 boundaries at triple junctions were examined, there was no crystallographic clustering associated with cracked boundaries.*

We also considered the sensitivity of cracking to the orientation which the boundary plane makes relative to the macroscopic direction of crack-propagation. Those boundaries which lie closest to the forward propagation direction are, as expected, most vulnerable to damage. Although clearly some cracking occurs in a sense opposite the forward cracking direction, no example was found making an angle greater than 120°, and most of the cracked boundaries exhibited angles less than 60°.

A Classification Scheme Representing the Data: It is quite evident that any classification which would be successful in predicting branching probabilities must consider the orientation of the grain boundary with respect to the nominal macroscopic crack plane and direction of crack propagation. We propose an augmented classification which takes into account a broader range of the salient features observed in the measured data set. We consider that all small-angle boundaries with absolute minimum disorientations less than 14°, and all Σ3 disorientations (regardless of the crystallographic character of the boundary plane) have the lowest probability of cracking. Denote this class of boundaries as class A. The experimental evidence suggests that other low-Σ boundaries in the range Σ5 - Σ29 may have lower probabilities for cracking than general high-angle boundaries, although insufficient experimental evidence exists to make a strong case. This second class of boundaries is labeled B. The third category is the category of other high-angle grain boundaries, and is labeled C. Furthermore, we have subdivided each category into three ranges of boundary plane angles: i ∈ (0,30°), j ∈ (31,60°), m ∈ (61,90°), n ∈ (91,180°). The classification suggested by the experimental record can be expressed as

$$P_{An} < P_{Am} < P_{Aj} < P_{Ai} < P_{Bn} < P_{Bm} < P_{Bj} < P_{Bi} < P_{Cn} < P_{Cm} < P_{Cj} < P_{Ci},$$

where, for example P_{Bm} denotes the probability of cracking a boundary found within the low-Σ category (type B), whose boundary plane falls in the range (61,90°) (subcategory m). Using this new classification scheme, 237 of the 277 triple junction decisions not involving the Σ3 boundary type were correctly predicted, or about 86%. If the entire set of 818 triple junctions is considered, this classification gives a 95% success rate. Failures of this classification set are usually associated with triple junctions where both branches fall in the same element of the classification set.

It is evident that considering the geometrical orientation of grain boundaries substantially improves the prediction of branching decisions at triple junctions. The classification set introduced above is still very coarse, and it is likely that refinements are possible. However, within the context of the limited data available, we concluded that further attention to refinement of the set would be of questionable value.

A Model for Intergranular Crack Propagation: Several approaches have been taken to the problem of modeling intergranular crack propagation. Several of these have been based upon the ideas of percolation theory. We have considered the framework for a class of models which overcomes the limitations of percolation theory, and which is capable of directly incorporating information from the ex situ damage record. In our model the location of the crack tip is determined by a Markov chain on the network representing the microstructure. The microstructure is modeled by a 2-dimensional network, although extension to a 3-dimensional network is straightforward. The process of crack propagation is Markovian since it is assumed that crack advance depends only upon the current location of the crack tip.

In the simplest case the two-dimensional grain-boundary network is modeled as a regular hexagonal array. Thus each grain is surrounded by six grain boundaries. Triple-points (where three grains meet) are called nodes. The lattice orientation of each grain, and the (geometrical) structure of each grain boundary is presumed known. Thus, the hexagonal network is used only to specify connectivity of the grain boundaries in the network, and not any other geometrical relationship such as grain boundary inclination with respect to the stress axis. We wish to predict the most likely paths the crack tip will take in propagating through this network.

We define the following state variables:

- q_i^T — The probability that the crack tip is at GB (grain boundary) i at timestep T.
- $q_i^{(0)}$ — The probability that the crack starts at GB i.
- P_{ij} — The probability that the crack will move to GB i at time $t = k$, given that it is at j at time $t = k\text{-}1$.

P_{ij} are the elements of the "transition matrix", P. We make the following assumptions: (i) the path of the crack tip is continuous, and (ii) the crack propagates from one side of the network to the other; i.e., without doubling back on itself. The reason for the second assumption is the difficulty in interpreting the direction of crack propagation without this restriction. For example, how does one interpret the motion of a crack tip from GB i to GB j and then back to GB i ? Although this assumption is indeed a restriction on observable phenomena, it is consistent with most observations of crack propagation.

It is clear that the matrix P contains all of the information about the grain boundary structure, including the connectivity of the grain boundaries and their resistance to cracking. Although the details cannot be presented here, the main result can be expressed in the following form:

$$C^{(T)} = q^{(0)} + \begin{pmatrix} (A-D)\sum_{k=0}^{T} A^k q \\ \\ B\sum_{k=0}^{T} A^k q \end{pmatrix}$$

where $C_i^{(T)} = \{\text{prob that } i^{th} \text{ GB cracks on or before timestep } T\}$. In this expression A, B and D depend only upon the transition probability matrix P.

A few results obtained from implementation of the model are described for the case where transition probabilities have been assigned more-or-less randomly to the idealized network. The procedure is as follows: A variable fraction of the grain boundaries were selected to be terminal. Other (non-selected) grain boundaries are assigned random probabilities in the range (0,1). The diagonal elements of P are then calculated, using renormalization if necessary. An initial distribution of cracks (q_0-vector) is assigned. Crack propagation is observed by iterating the action of P on q_0. The final probability vector is also calculated using the relation above.

When a random assignment of the transition probabilities was selected for all but the precracked boundaries, it was evident that multiple branches of crack propagation occur. When 20% of the horizontal boundaries (i.e., perpendicular to the applied stress) of the network were randomly assigned to be terminal, crack propagation is severely restricted in this case. When 60% of the non-horizontal (120°) boundaries (i.e., those not perpendicular to the stress axis) are randomly selected to be terminal (with the remaining boundaries assigned random probabilities), crack propagation is far more extensive. *It is evident from these limited simulations that crack propagation is predicted to be very sensitive to the details of connectivity in the grain boundary network, and also to the bias introduced by the stress state (nominally a vertical tensile stress in these simulations).*

Summary Remarks

We have examined the microstructure of a sample of Inconel Alloy X-750 damaged by ISCC, after fatigue precracking, in a high-temperature environment of deaerated water. The main focus of the study has been to study potential correlations between the geometrical structure of grain boundaries and their propensity for cracking. Using OIM, coupled with calibrated serial polishing, all five geometrical parameters of grain boundary structure were estimated. Four of these angular parameters can be measured to an uncertainty of about 1°, but the angle of inclination of the boundary could only be estimated to an accuracy of about 9°.

Regarding the ex situ record of ISCC propagation in the material, we find that general high-angle boundaries are most susceptible to cracking, given that the direction of forward crack propagation of the macroscopic crack lies within about 120° of the local crack plane. Small-angle (absolute minimum disorientation < 14°) and Σ3 grain boundaries were not observed to crack, regardless of the orientation of the local plane with respect to the forward crack direction. This observation is all the more significant in light of the observation that a broad distribution of plane-normals is observed for Σ3 grain boundaries. Some CSL boundaries lying in the range Σ5 - Σ49, purely on the basis of lattice disorientation, were found to crack; however, when the crystallographic character of the crack plane, and/or the more restrictive disorientation criterion of Palumbo and Aust are considered, the evidence suggests that very few (if any) true CSL boundaries in this range actually cracked. These observations are in harmony with the earlier studies of Palumbo and Aust [1] and Crawford and Was [2] on other nickel-based materials which did not explicitly consider the orientation of the grain boundary plane.

On the basis of the data collected in these observations, an ordering of the susceptibilities to ISCC damage was proposed (embodied in inequality above). This ordering classification takes into account both the lattice misorientation and the inclination of the grain boundary relative to the nominal forward cracking direction. All boundaries have been classified into one of twelve categories. On this basis the branching decisions at 95% of the observed triple junctions along the crack path are correctly predicted. It is evident that a finer classification could probably be devised which would have an even higher success ratio; however, with the current experimental limitations in measuring grain boundary inclination angles, and the limited number of triple junctions observed along the advancing crack (818 in the present study) it is not likely that great improvement could be achieved.

We have proposed a model to predict the crack path for ISCC based upon the ex situ record of damage probabilities. The essential aspect of this 2-dimensional model is that the cracking is modeled as a Markov chain on a regular hexagonal array of grain boundaries representing the connectivity of the network. The model is Markovian because the path of crack propagation is dependent only upon the arrival of the crack at the neighboring (connected) boundary. The model enables two kinds of predictions: (1) the probability the the crack ends on any particular grain boundary within the network, and (2) the probability that any given grain boundary within the material will be cracked. A simple thresholding operation on this latter probability enables a prediction of the crack path. Asymptotic expressions in the limit of long time exposures are available for both predictions.

Applications of the model to simulated microstructures clearly show the importance of the initiation phase of cracking, the importance of the distribution of grain boundary types (i.e., susceptibility to fracture) and the sensitivity of the results to the details of connectivity. The model can easily be extended to 3-dimensional crack paths, and to network connectivities more realistic than the hexagonal one examined here.

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