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Abstract

The introduction of gaseous environments such as humid air, hydrogen and oxygen, and mixtures of gases strongly influences the fatigue crack growth rate of structural alloys. The observed changes in fatigue crack growth rate are discussed in relation to dislocation impurity transport and the crack closure concept. Significant changes in the plastic behavior near the crack tip are described and related to the fatigue crack growth behavior. A wide range of experiments aimed at evaluating the overall interaction between the gaseous environment and the propagating fatigue crack are described.

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Introduction

The influence of environment on fatigue crack growth has been recognized for a long time. The mechanism by which this environmental interaction occurs has still not adequately been established. This paper will discuss many aspects of the influence of gaseous environments on the fatigue crack growth of structural alloys.

In order to establish if there is an environmental effect a baseline environment must be established. For this purpose either a dry inert gas or a good vacuum is acceptable. In many of the studies to be described here a vacuum of less than 10^{-5} Pa is used as the baseline environment. The problem of rewelding exists in a good vacuum but there is no strong evidence that the rough fatigue surfaces do reweld significantly. When vacuum growth rates are compared to growth rates in other inert environments little difference is observed.

The aggressive gaseous environments that influence the

fatigue crack growth rate include humid air on aluminum, titanium and iron base alloys [1-12], hydrogen and hydrogen sulfide on iron, nickel and titanium base alloys [4,5,10, 13-18], dry oxygen on aluminum, nickel, titanium, and iron base alloys [4,5,10,16,19]. In many of these studies the impact on the fatigue crack growth rate due to the interaction between these gases is evaluated. This paper will discuss several aspects of the interaction of the gaseous environment with the propagating fatigue crack. The main emphasis will be on the materials and environments the author has been investigating.

Effects of Environment

There are several stages to the environmental influence on fatigue crack growth. The first is that the gas must adsorb to the surface of the material. A schematic of the adsorption process is given in Figure 1 for hydrogen on a metal surface. Many processes are taking place simultaneous-

Figure 1 Schematic of Hydrogen Gas Adsorption on a Clean Metal Surface



ly; molecular physical adsorption, possibly molecular chemical adsorption, dissociation, recombination. These processes that have been discussed previously in some detail [14] for hydrogen will apply for any active gas. The main point to be made here is that if the gaseous molecule does not adsorb and dissociate it will not influence the fatigue crack growth rate.

Dislocation Transport of Hydrogen

After the adsorption and dissociation of the gas has occurred the gas atom must be transported to the active sites in the vicinity of the crack. This can be accomplished by normal bulk or surface diffusion or by some other process such as pipe diffusion or dislocation transport [20-25]. The extra depth possible with the dislocation transport of hydrogen has been estimated [26] and shown to be many times the depth expected from diffusion for loading frequencies in the 0.1 to 60 Hz range for both iron and nickel base

materials. It is this enhanced hydrogen transport that has been used to explain the applied stress intensity range dependence of the fatigue crack growth rate and corresponding intergranular fracture mode. An example of this dependence is given in Figure 2 for the HP-9Ni-4Co-0.2C steel [20].

Figure 2

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The Dependence of the Hydrogen Accelerated Fatigue Crack Growth Rate and Associated Fraction of Intergranular Fracture on Stress Intensity for HP-9Ni-4Co-0.2C Steel [20]



What is shown is that to get the enhanced growth rate and corresponding increase in intergranular fracture mode the forward yield plastic zone size must be a reasonable fraction of the prior austenite grain size. The growth rate is maximum when the forward yield plastic zone size is approximately the prior austenite grain size and then decreases as the plastic zone size increases. The fracture path is totally transgranular when the reverse yield plastic zone size is of the order of the prior austenite grain size. Similar correlations between the change from intergranular to transgranular fracture when the reverse yield plastic zone size approaches the grain size have been reported for titanium [28] and humid air or steel [29].

A proposed explanation for the intergranular failure is that the hydrogen is swept to the grain boundaries, interacts and localizes with the impurities at the grain boundaries to lower the local fracture energy. If there were no impurities present at the grain boundaries then intergranular failure would not be expected [27]. Since the hydrogen would not be expected to be trapped at clean grain boundaries it is easy to understand why the martensite lath interfaces would not be preferentially fractured but the prior austenite grain boundaries would be. The change to transgranular mode occurs

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when the reverse plastic zone size is such that it destroys the continuous path represented by the prior austenite grain size.

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An additional factor in the hydrogen influence on fatigue crack growth is its temperature dependence. An example is shown in Figure 3 for the same HP-9Ni-4Co-0.2C steel [16]. In this case there is a good correlation



between the increase in crack growth rate and the amount of intergranular failure. A similar correlation was reported for nickel base alloys [30]. The intergranular failure mode enhanced fatigue crack growth rate cannot be a general correlation for steel since many steels that show a large hydrogen effect on fatigue crack growth rate exhibit a transgranular failure mode [5,16]. It may still be that the transgranular fracture mode is associated with hydrogen being transported to interphase boundaries, such as at carbides, which would be rich in impurities and serve as traps for the hydrogen. This would then lead to a lower fracture energy path, albeit it would be discontinuous but closely spaced.

A proposed explanation for a similar temperature maximum

observed during sustained loading of steel in hydrogen has been the influence temperature has on the dissociationrecombination process [31]. An alternative explanation for the temperature dependence of the fatigue crack growth intergranular failure mode and possibly the transgranular mode would be that the hydrogen transport would be greatly reduced at the higher temperatures. This would result in less hydrogen at the grain boundaries with less tendency to fracture there. For the nickel base alloys a temperature dependence hydrogen effect resulting in serrated yielding has been reported [32-35]. The low temperature effect was related to reduction in hydrogen diffusion rate and the high temperature disappearance of the effect is postulated to be due to the reduction in the hydrogen-dislocation interaction. Although the temperatures reported were appreciably lower than for the fatigue crack growth studies the high local deformation at the crack tip would be expected to reduce the mobilities of the mobile dislocations thereby requiring less interaction energy for the hydrogen to be able to stay associated with the dislocation transport would be severely curtailed and the reduction of embrittlement would be observed.

Combined Gas Effects with Hydrogen

The significant increase in fatigue crack growth rate in pure hydrogen gas can be significantly altered by the presence of secondary gases. An example of this is given in Figure 4 for the HP-9Ni-4Co-0.2C steel [16]. This result



is also characteristic for other steels [5,16]. What is observed in these studies is that pure hydrogen gas greatly enhances the fatigue crack growth rate. Addition of oxygen, water, carbon monoxide, and nitrous oxide to the hydrogen tends to inhibit the hydrogen effect. This is explained by the preferential adsorption and dissociation of these gases on the fresh metal surfaces preventing dissociation of the hydrogen. Addition of methane, carbon dioxide, and natural gas has very little influence on the hydrogen effect. Addition of hydrogen sulfide to the gaseous hydrogen significantly increases the hydrogen effect [5,17]. A reverse effect of oxygen was noted for nickel cobalt alloys tested in oxygen mixed with hydrogen [18]. It was observed that the combined oxygen-hydrogen environment showed higher fatigue crack growth rate than the pure hydrogen. In this case it was established that the observed grain boundary failure was associated with an excessive amount of segregated sulfur and this sulfur-rich fracture surface is the location for the subsequent gas adsorption. The explanation of the result is schematically shown in Figure 5 where the presence of sulfur on the grain boundary fracture surface acts as a poison to hydrogen recombination, greatly enhancing the local hydrogen activity. This is also the explanation for

Figure 5

Schematic of Adsorption of Hydrogen on S Contaminated Metal Surface Showing Enhanced Hydrogen Dissociaton

the strong influence of hydrogen sulfide. The introduction of oxygen does not displace these sulfur occupied active sites for hydrogen dissociation. This clearly demonstrates that trends in gaseous environmental interactions with fatigue crack growth may reverse themselves when a metallurgical condition changes.

Humidity Effects

Humid air influences the fatigue crack growth behavior in both aluminum [1,3,6,7,8,10] and iron base alloys [2,5,10,11]. The nature of the interaction seems to be a significant modification of the local crack tip plastic behavior. In a study using electron channeling to probe the plastic behavior at the crack tip of a low carbon steel [2] the extent of subcell formation is shown to be much less when fatigue takes place in humid air than in dry nitrogen. A representative difference in the amount of crack tip

plastic deformation and residual crack tip opening displacement is shown in Figure 6 [2]. Similar results are shown



Positive Replicas of the Crack Type Underload at $\Delta K = 11 \text{ MPa}\sqrt{m}$ in (a) Moist Air and (b) Dry Nitrogen [2]

for the early stages of fatigue crack growth of aluminum alloy when comparing dry and humid environments [3,6]. In all cases a large decrease in local crack tip plastic behavior is observed with a resulting decrease in residual crack opening displacement when fatigue crack growth takes place in a humid environment.

In studies on 2024 Al [36] and 7075 Al [37] it was proposed that the changes in fatigue crack growth rate between humid air and an inert environment for aluminum might be explained by the crack closure concept [38,39]. Direct measurement of the crack closure load on part through cracked specimens using ultrasonic techniques showed that the closure load was reduced in a humid environment. This reduction was sufficient so that a plot of crack growth rate versus the effective stress intensity range calculated using the crack closure model accounted for all the shift in growth rate. The change in crack closure is associated with a reduced residual equivalent strain on the fracture surface. The equivalent strain is associated with the increased dislocation density, shear effects at the edges, and the surface roughness. The results described earlier [2,3,6] all support the idea that this is occurring. Recently studies on 2024-T3 Al clad and 7075-T6 Al clad [1] for similar exposures did not show the same results. In fact there was no observed difference in crack closure load although a significant difference in fatigue crack growth was observed. Unfortunately direct comparison of the results is not

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realistic due to the fact that the second study [1] used relatively thin sheet, 1-6 mm., and the sheet was Al clad. Nonetheless, the divergent results require a more in-depth evaluation of the influence of humid air on the fatigue crack growth. The question that arises is does a reduction in closure load with the concomitant increase in effective stress intensity range explain the increase in growth rate? All the evidence seems to support a reduction in plastic deformation which would be consistent with a reduced strain at fracture. This reduced strain at fracture would result in a lower residual strain on the fracture surface and the lower crack closure load. It seems that the reduced strain to failure itself could be used as the explanation for the increased fatigue crack growth, with the change in closure load a consequence but not a cause. Further studies are necessary to attempt to evaluate this chicken-and-egg effect.

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Oxygen Influence on Fatigue Crack Growth

It is known that oxygen increases fatigue crack growth rate in nickel, titanium, iron, and possibly aluminum base alloys [4,5,10,16,19]. In an attempt to understand this change in crack growth rate in oxygen the following experiments were performed [19]. Figure 7 shows a compact tension specimen used for the experiments. The fatigue crack was



first grown in a 1.3 µPa vacuum as indicated on the crack surface and then the chamber was backfilled with 10 kPa of oxygen-18 and the fatigue crack growth continued. Oxygen profiles normal to the fracture surface as determined by inert ion sputtering would then be determined by Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS). The oxygen-18 was used to assist in the SIMS analysis. Experiments were performed on Monel 404, commercially pure titanium, 7075-T651 and 2219-T87 aluminum alloys. In all cases an increase was noted in fatigue crack growth rate for the oxygen-18 environment. The change in growth rate ranged from the statistically insignificant ratio of

growth rate in oxygen to that in vacuum of 1.1 for the 2219-T87 to a ratio of 5.5 for the Monel 404. It was expected that the oxygen concentration profile normal to the fracture surface formed in vacuum represents normal oxidation and diffusion when exposed to the oxygen-18 after fatigue crack growth. The fatigue crack fracture surface profile for the segment formed in oxygen-18 would be representative of oxidation, diffusion, and any additional oxygen transport mechanism occurring during the fatigue crack propagation. The inert ion sputtering profiles as determined by AES and SIMS in all cases show a significant enhancement of the thickness of the oxygen-rich region for the region where the fatigue crack growth was in the oxygen-18. Figure 8 is the AES depth profile for the Monel 404, Figure 9 the AES depth profile for the 2219-T87, and Figure 10 the SIMS depth profile for the commercially pure titanium. An accurate



inert ion sputtering rate was not determined. Using an estimate of from 5 to 10 nanometers for the natural oxide thickness gives an estimate of the enhanced transport of 10 to 60 nanometers. Metallographically polished specimens that were oxidized at room temperature gave identical



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sputtering profiles to those fatigued in vacuum. This result implies that the observed differences between samples run in vacuum and in oxygen-18 would not be due to differences in surface roughness between the vacuum and oxygen fracture surfaces.

The interpretation given for the results is that in all cases significant transport of oxygen into the bulk takes place during fatigue crack growth in the oxygen environment. The increased oxygen level has a different influence on each of the materials. The Monel 404 and commercially pure titanium behave as if a significant change in plastic behavior takes place. It has been shown that an increase in oxygen in solid solution in a titanium alloy in a structure where oxygen strengthens the alloys results in an increase in fatigue crack growth rate [40]. A definite change in fracture morphology is seen in the Monel 404. For the aluminum alloys the enhanced oxygen depth has little if any influence on fatigue crack growth rate. This result indicates that hydrogen must play a role in the humid air effect. The oxygen effects again can be modeled by the reduction in strain at fracture, resulting in a reduced residual crack closure strain. But again the two effects cannot be separated. It may be that the ideas of how the environment changes the near surface plastic behavior [41] need to be incorporated into the fatigue crack growth thinking.

Summary

In this paper a discussion of various aspects of gaseous environmental influence on fatigue crack growth in structural alloys was described. All the evidence points to an influence of the environment on the local plastic behavior of the alloys. In many cases this is associated with enhanced transport of the atoms during the fatigue crack growth cycling. Unfortunately so many different aspects influence the fatigue crack growth rate, including loading conditions, sample thickness, sample geometry, loading frequency,

environmental pressure, temperature, microstructure, grain size, alloy chosen, impurities in both the metal and the gas phases, that any study only looks at a very small segment of the total picture. The differences in the segment each set of investigators looks at makes it difficult to correlate many of the results. In spite of this the past decade has qualitatively cleared up much of the mystery of the environmental influence on fatigue crack growth, but the details of the plastic behavior modifications and the direct reductions in cohesive energy and the interactions between the two as determined by the environment are still to be established.

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