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MASTER

INFLUENCES OF GASEOUS ENVIRONMENT ON LOW GROWTH-RATE FATIGUE CRACK PROPAGATION IN STEELS

by

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NOTICE

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FOREWORD

This report summarizes work performed during the initial year of the program, commencing May 1, 1979. The research was administered under contract No. DE-AC02-79ER10389.A000 by the Office of Basic Energy Sciences, U.S. Department of Energy, with Dr. Stanley M. Wolf as Program Monitor. The work was performed under the direction of Professor Robert O. Ritchie as principal investigator, with assistance from graduate students S. Suresh and J. Toplosky, and undergraduate Helen Conley.

ABSTRACT

The influence of gaseous environment is examined on fatigue crack propagation behavior in steels. Specifically, a fully martensitic 300-M ultrahigh strength steel and a fully bainitic 2¼Cr-1Mo lower strength steel are investigated in environments of ambient temperature moist air and low pressure dehumidified hydrogen and argon gases over a wide range of growth rates from 10^{-8} to 10^{-2}mm/cycle, with particular emphasis given to behavior near the crack propagation threshold ΔK_o. It is found that two distinct growth rate regimes exist where hydrogen can markedly accelerate crack propagation rates compared to air, i) at near-threshold levels below ($5x10^{-6}$mm/cycle) and ii) at higher growth rates, typically around 10^{-5}mm/cycle above a critical maximum stress intensity K^T_{max}. Hydrogen-assisted crack propagation at higher growth rates is attributed to a hydrogen embrittlement mechanism, with K^T_{max} nominally equal to K_{Iscc} (the sustained load stress corrosion threshold) in high strength steels, and far below K_{Iscc} in the strain-rate sensitive lower strength steels. Hydrogen-assisted crack propagation at near-threshold levels is attributed to a new mechanism involving fretting-oxide-induced crack closure generated in moist (or oxygenated) environments. The absence of hydrogen embrittlement mechanisms at near-threshold levels is supported by tests showing that ΔK_o values in dry gaseous argon are similar to ΔK_o values in hydrogen. The potential ramifications of these results are examined in detail.

1. INTRODUCTION

The current uncertainty in foreign crude oil supplies to this country has prompted renewed interest in our coal resources as a viable major energy source. Although the technology for extensive utilization of this coal is now rapidly emerging, many materials-related problems still remain, both on the basis of economics and from the point of view of increased reliability. Challenges to the materials community in this regard now lie in the search for less expensive materials capable of improved performance in the presence of mechanically and chemically hostile environments. Coal gasification and liquefaction processes, for example, both involve the use of welded steel pressure vessels, as large as 60 m high, 6 m in diameter with 250-350 mm wall thicknesses, which must operate continuously, economically and, above all, safely, at high pressures and temperatures in the presence of erosion-producing solid particles, and chemically-aggressive atmospheres containing hydrogen and hydrogen sulfide gases, etc. Design of such vessels must allow for the fact that sub-critical growth of crack-like defects, which invariably are present in such large-scale structures, may be vastly accelerated by the presence of such environments, particularly those containing (or producing) hydrogen. The principal focus of the present program is a fundamental study of the influence of gaseous environment on sub-critical crack growth by fatigue, with particular emphasis on influences of hydrogen on crack propagation at ultralow, near-threshold growth rates (less than 10^{-6} mm/cycle) in both high strength and low strength steels.

Fatigue crack propagation in general is characterized in terms of the alternating stress intensity ΔK through expressions of the form[1]:

$$\frac{da}{dN} = C \Delta K^{m} \qquad (1)$$

where da/dN is the crack growth increment per cycle, ΔK is given by the difference between the maximum and minimum stress intensities for each cycle, i.e. $\Delta K = K_{max} - K_{min}$, and C and m are scaling constants. This expression adequately describes behavior (in the absence of environmental effects) at the so-called mid-range of growth rates, typically 10^{-5} to 10^{-3} mm/cycle, but may severely underestimate rates at higher growth rates as K_{max} approaches K_{Ic}, the fracture toughness, (or, when limit load is exceeded) and is conservative at much lower growth rates (i.e. less than 10^{-6} mm/cycle) as ΔK approaches the threshold stress intensity, ΔK_o, below which cracks remain dormant or grow at experimentally undetectable rates (Fig. 1). Whereas a large body of information exists for behavior at intermediate and high growth rates, behavior patterns for fatigue crack propagation at near-threshold levels have only recently become apparent[2]. It has been found in high strength steels, for example, that near-threshold crack propagation rates are accelerated, and the value of ΔK_o decreased, by such factors as increasing load ratios, increasing strength level, finer microstructures, and prior impurity-induced embrittlement[2-6]. Similar results on lower strength steels[7], titanium[8] and aluminum[9] alloys broadly reflect these trends. Models to explain such data are relatively scarce, although Ritchie[2,4] has proposed that, for high strength steels at least, such behavior can be rationalized in terms of environmental effects, which in this case pertain to hydrogen embrittlement mechanisms resulting from crack tip reactions with moisture in air. Data to support such environmental interactions at near-threshold levels, however, are in certain instances somewhat contradictory. Where growth rates have been compared between air and vacuum, significant environmental accelerations have invariably been observed,[10-13] but for tests conducted in air, water and argon atmospheres often no effect has been seen[14-16] and, in certain cases, the seemingly more aggressive environment has resulted in slight decelerations in growth rates.[17,18] Whereas certain of these observations could be the result of "impure" inert atmospheres[11], they do present contradictory evidence for the environmental model[2,4]. One of the principal objectives of the present program is to demonstrate unambiguously the influence of environment on near-threshold behavior by a comparison of crack propagation rates in carefully controlled environments of moist air, inert gas, vacuum and hydrogen gas. Both high and low strength steels are chosen for study because of their markedly different sensitivity to environmentally-induced cracking (i.e. hydrogen embrittlement), at least under monotonic loading.

This report summarizes the progress of the first nine months of the program. Studies have been performed on two materials, a fully martensitic

300-M ultrahigh strength steel, tempered to two strength levels, and a thick-section, fully bainitic 2¼Cr-1Mo low strength steel (ASTM A542 Class 3). Testing has principally involved the generation of fatigue crack propagation data (covering six decades of growth rates from 10^{-2} to 10^{-8} mm/cycle) and associated fractography in atmospheres of ambient temperature moist air, dry argon and dry hydrogen gas as a function of cyclic frequency and load ratio. Preliminary studies have also been instigated to monitor hydrogen transport rates in both structures, in both unstressed and plastically deformed smaples, using electrochemical permeation measurements. From the results obtained, a radically new interpretation of the influence of environment on near-threshold fatigue crack propagation behavior in steels is suggested which, if substantiated, may have significant consequences on the potential use of steel structures for coal conversion, hydrogen storage, and hydrogen transport systems.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Two alloy steels were investigated during the first year of the program, namely 300-M quenched and tempered to yield strengths of 1737 and 1074 MPa, and ASTM A542 Class 3, quenched and tempered to a yield strength of 500 MPa. Chemical compositions in weight percent are listed in Tables I.

The ultrahigh strength 300-M steel (essentially AISI 4340 modified with 1.4% silicon) was of aircraft-quality (vacuum-arc remelted) and supplied in the form of fully-annealed hot-rolled bar. Material was austenitized at 870°C for 1 hour, quenched into agitated oil, and tempered for 1 hour at 300°C* and at 650°C. These treatments will be hereafter referred to as 300M-T300 and 300M-T650 respectively. Both microstructures were fully martensitic with a prior austenite grain size of 20 μm; evidence of ε-carbide precipitation and roughly 4% retained austenite as interlath films were observed in the T300 structure, whereas spheroidized cementite was present in the T650 structure with no evidence of retained austenite.

The lower strength 2¼Cr-1Mo steel was supplied as a 175 mm thick plate from Lukens Steel Co., conforming to the ASTM A542 Class 3 standard and

*the commercially-used heat-treatment

hereafter referred to as SA542-3. The plate had been austenitized at 950°C for 5½ hr, water quenched and tempered at 663°C for 7 hrs, before stress-relieving for 15 hrs at 593°C, 22 hrs at 649°C, and 18 hrs at 663°C. Microstructures and properties of this plate varied only marginally with through-thickness position, the structure being predominately bainitic with less than 3% free polygonal ferrite at center thickness. Bainite grain sizes were measured between 60 to 70 μm[19]. Ambient temperature mechanical properties of both steels are listed in Table II.

2.2 Fatigue Crack Growth Testing

Fatigue crack propagation tests were performed using 12.7 mm thick ASTM standard 1-T compact specimens, of L-T orientation for 300-M and T-L for SA542-3. Specimens were cycled under load control on 50kN Instron electro servo-hydraulic testing machines under sinusoidal tension over a range of load ratios ($R = K_{min}/K_{max}$) from 0.05 to 0.75 with cyclic frequencies varying between 0.5 and 50 Hz. Crack lengths were continuously monitored using DC electrical potential systems,[19] capable of measuring absolute crack length to within 0.1 mm, and to detect changes in crack length of the order of 0.01 mm. Growth rates in excess of 10^{-5}mm/cycle were generated under constant load (increasing K) conditions. Lower growth rates were determined using both load-shedding (decreasing K) and load increasing (increasing K) conditions. Crack propagation threshold, ΔK_o , defined in terms of a maximum growth rate of 10^{-8}mm/cycle (4×10^{-10}in./cycle), were approached using a procedure of successive load reduction (by not more than 10%) followed by crack growth. At each load level, growth rate measurements were taken over increments of 1 to 1.5 mm, representing more than four times the previous cyclic plastic zone size. Following ΔK_o measurements, loads were increased in steps and the same procedure followed. Plane strain conditions were maintained throughout, based on the criterion that cyclic plastic zone sizes did not exceed one-fifteenth of the specimen thickness. All tests were performed at ambient temperatures in carefully controlled environments of moist air (30% relative humidity), dehumidified ultrahigh-purity hydrogen gas (138 kPa pressure) and dehumidified ultrahigh-purity argon gas (138 kPa pressure). Input gases to the environmental chamber, which was mounted locally on the specimen, were rigorously purified through the use of molecular sieves and liquid nitrogen cold traps.* A modified system is

*Liquid nitrogen cold traps cannot be used for argon since the gas freezes above -196°C. For this reason, future inert gas testing will involve helium.

currently in use which allows prior evacuation and bake-out of gas lines. A more complete description of the environmental near-threshold fatigue test procedures can be found elsewhere[20].

2.3 Accelerated K_{Iscc} Testing

Thresholds for sustained-load stress corrosion cracking, K_{Iscc}, in gaseous hydrogen were estimated using the accelerated rising-load procedure of Clark and Landes[21]. Standard 12.7 mm thick compact specimens, fatigue pre-cracked to a crack length-to-width (a/W) ratio of 0.5 at a stress intensity below $15MPa\sqrt{m}$ (R=0.05), were loaded in air and 138kPa dry hydrogen gas at a fixed displacement rate corresponding to an initial elastic stress intensity rate ($\dot{K}$) of 0.1 $MPa\sqrt{m}$/sec. K_{Iscc} values were estimated using J-integral measurements where the load/load-line displacement record in hydrogen showed significant departure from the base-line air record (Table II). The values quoted in Table II must only be taken as approximate because of the rapid $\dot{K}$ rates utilized, and the approximate nature of the test procedure. We are currently repeating these measurements using an order of magnitude slower displacement rates.

2.4 Hydrogen Permeation Measurements.

Experiments to measure rates of hydrogen transport in both steels utilized the electrochemical permeation procedures of Kurkela and Latanision[22], based on the technique of Devanathan and Stachurski[23]. A schematic diagram of the hydrogen permeation cell used is shown in Fig. 2. The material under investigation is made a bi-electrode in the form of a membrane (about 1.5 mm in thickness) and clamped between the cathode (hydrogen entry) and anode (hydrogen exit) half-cells exposing 1.27 cm^2 of surface area. An electrolyte solution of 0.1 N H_2SO_4 is used in the cathode half-cell and 0.1N NaOH in the anode half-cell. To minimize the effects of oxygen reduction, both solutions are de-aerated prior to and during the experiment by bubbling nitrogen gas. Hydrogen charging is controlled by a galvanostatic circuit which insures that the cathodic charging current is a function of the external resistance and not the cell resistance. Hydrogen is absorbed into the membrane and diffuses through to the other side. The anodic side of the specimen is maintained at a constant potential versus a saturated calomel electrode by a potentiostat so that the concentration of hydrogen on that surface is zero. Thus, when hydrogen emerges at the anodic side, it is immediately oxidized and the current generated thereby is a direct measure of the permeation rate. To make sure that the oxidation of hydrogen is the sole reaction, the anodic side is plated with palladium to suppress the oxidation of iron (this has no effect on the permeation behavior). The permeation current is measured by an electrometer and recorded on chart paper. All experiments are carried out at room temperature.

To study permeation in specimens undergoing plastic deformation, a tensile specimen (design shown in Fig. 3) with an exposure area of 0.3 cm^2 will be used and the same technique adopted. The specimen-cell assembly is positioned between the crossheads of an Instron machine. The specimens are to be deformed at a constant extension rate and simultaneously charged with hydrogen. Permeation currents and stress-strain curves will be recorded.

3. RESULTS TO DATE

3.1 Hydrogen Transport Studies in 300-M and 2¼Cr-1Mo steel.

The objective of this phase of the program is to measure the relative rates of hydrogen transport in the various microstructures under investigation, both in unstressed samples to gather diffusion data and in samples undergoing plastic deformation at varying strain rates to determine possible dislocation-aided[25] transport data. The rationale for these studies are several-fold. We wish to examine whether the varying susceptibility of certain steels and certain microstructures can be related to transport factors, i.e. does hydrogen transport ever become rate-limiting for hydrogen-assisted failure. In fact, for lower strength steels where mechanisms for such fracture are largely unknown, it is uncertain at this stage whether hydrogen transport in the iron matrix plays a role since the "embrittlement zone" may be very close to the crack tip, rather than some distance (approximately two crack tip displacements*) into the material, as is often modelled for high strength steels. In addition, as described below, the effective threshold stress intensity for environmentally-assisted failure in fatigue by hydrogen embrittlement is significantly less than

* representing the point of maximum dilatation.

K_{Iscc} in low strength, strain-rate sensitive steels. This suggests a strain-rate dependence on the environmental threshold, which is conceivably a consequence of hydrogen transport via dislocation-aided motion.

This study has only recently been started and initial experiments have been performed only on unstressed samples. A typical permeation transient for SA542-3 is shown in Fig. 4. By applying Fick's Law with appropriate boundary conditions, one can solve for the diffusion coefficient for hydrogen using

$$D_H = \frac{0.138\ L^2}{t_{1/2}} \qquad (2)$$

where D_H is the diffusion coefficient of hydrogen in cm^2/sec, L the membrane thickness in cm, and $t_{1/2}$ the half time of the permeation current transient in seconds. Using such analyses, the diffusion coefficient in SA542-3 was found to be $5.5 \times 10^{-7}\ cm^2/sec$, in agreement with published values.[24]

3.2 Fatigue Crack Propagation in Ultrahigh Strength 300-M Steel.

High strength steels, with yield strengths exceeding 1000 MPa, such as 4340 and 300-M, are generally regarded as being extremely susceptible to hydrogen embrittlement based on the fact that their K_{Iscc} thresholds for sustained load cracking are often small compared to K_{Ic}.[26] Under cyclic loading, there is now ample evidence for a similar susceptibility to hydrogen embrittlement at intermediate growth rates.[26-32] However, no information has been collected to date on whether such hydrogen-induced embrittlement results in accelerated crack propagation at near-threshold growth rates below 10^{-6} mm/cycle.

The variation of fatigue crack propagation for 300-M is shown in Fig. 5 for a range of tempering temperatures and strength levels. These data, from the previous work of Ritchie[3], were obtained for a load ratio of 0.05 at 50 Hz frequency in an atmosphere of ambient temperature moist air. It is very apparent that a reduction in the tensile strength from 2300 to 1200 MPa by increasing the tempering temperature, while producing little variation at intermediate levels, results in a significant reduction in near-threshold growth rates (by almost 3 orders of magnitude at $\Delta K = 9\ MPa\sqrt{m}$), and an increase in threshold ΔK_o values from 3 to 8.5 MPa$\sqrt{m}$. Results at high load ratios of $R = 0.70$ show similar trends although the magnitude of the differences were very much smaller[4].

In the present study we are examining the structures tempered at 300°C (T300) and 650°C (T650) in moist air, hydrogen gas, and inert atmospheres to investigate environmental effects. Initial tests have been conducted on the T300 structure at 50 Hz frequency with load ratios of 0.05 and 0.30 in both moist air and dehumidified hydrogen gas. The results obtained so far are shown in Figs. 6 and 7. It is apparent from Fig. 6 that at $R = 0.05$ at 50 Hz, there is little significant difference between growth rates in moist air and dry hydrogen, except for a slight increase due to hydrogen above 10^{-4}mm/cycle. By increasing the load ratio (Fig. 7), the threshold is decreased somewhat as expected, but more importantly an enhancement due to hydrogen can be observed at intermediate growth rates in the form of a sharp acceleration above a K_{max} value of approximately 20 MPa$\sqrt{m}$. This value of K_{max}, where hydrogen-assisted growth becomes readily apparent, hereafter referred to as K^T_{max}, corresponds approximately to typical values of K_{Iscc}, the threshold for hydrogen-assisted growth under monotonic loading for 300M-T300.[29,35] Such behavior is consistent with the concept of "stress-corrosion fatigue"[30], where the environmentally-assisted fatigue crack propagation can be considered in terms of (sustained-load) stress corrosion cracking and mechanical fatigue components which are either additive[27] or mutually competitive[28].

Preliminary fractographic results indicate no change in fracture mechanism due to hydrogen at near-threshold and at higher growth rates; a fine-scale transgranular mode with isolated intergranular facets is observed for both environments. Macroscopically, little corrosion deposit can be observed on near-threshold fracture surfaces in either atmosphere.

Summarizing the limited data obtained so far on ultrahigh strength 300M-T300 steel, dry hydrogen gas appears only to accelerate fatigue crack propagation rates (with respect to air at 50 Hz) above a critical K_{max} value approximately equal to K_{Iscc}. Thus, for a steel/heat-treated condition which is generally considered to be very susceptible to hydrogen embrittlement (under sustained loads), it is clear that the presence of dry hydrogen gas has <u>no significant effect</u> on ΔK_o or on near-threshold growth rates.

3.3 Fatigue Crack Propagation in Lower Strength 2¼Cr-1Mo Steel (SA542-3).

Alloy steels with yield strengths below 1000 MPa, such as 2¼Cr-1Mo, are generally considered to be relatively immune to hydrogen embrittlement based on their high K_{Iscc} thresholds for sustained load cracking[20,31,32]. Under cyclic loading, however, recent data in this laboratory and elsewhere have shown that fatigue crack growth in these steels can be considerably enhanced due to the presence of gaseous hydrogen at stress intensities well below K_{Iscc}[20,31,32].

In the present program, bainitic SA542-3 2¼Cr-1Mo steel has been tested at load ratios between 0.05 and 0.75 at cyclic frequencies between 50 and 0.5 Hz in ambient temperature moist air and dry hydrogen. Results at low mean stresses (R = 0.05) are shown in Fig. 8 for a range of frequencies, and in Fig. 9 at 50 Hz for a range of load ratios. It is apparent from these data that, by comparing crack growth behavior in air and hydrogen in the lower strength steels, two distinct regimes exist where hydrogen-assisted fatigue crack propagation can occur, namely at intermediate growth rates, typically above 10^{-5} mm/cycle, and (unlike ultrahigh strength steels) at near-threshold levels below 5×10^{-6} mm/cycle, as shown schematically in Fig. 10.

The major enhancement in crack propagation rates due to the presence of dry hydrogen gas can be seen below 5×10^{-6} mm/cycle where growth rates in hydrogen were as much as 100 times greater than in air and threshold ΔK_o values were reduced by as much as 27%. Similar results have been observed in normalized 2¼Cr-1Mo steels with lower strength ferritic/bainitic microstructures[20,32]. Increasing the load ratio R further increased growth rates (and lowered ΔK_o) in both environments, although the large acceleration due to hydrogen observed at R = 0.05 was practically nonexistent at R = 0.75 (Fig. 11). Reducing the frequency from 50 to 5 Hz did not appear to affect near-threshold rates. Fractographically, there was little difference between fracture mechanisms in air and hydrogen near ΔK_o despite the large influence of hydrogen on near-threshold growth. Below 10^{-5} mm/cycle, a fine scale transgranular mode was seen for both atmospheres with little evidence (10%) of intergranular facets (Fig. 12). Macroscopically, characteristic bands of corrosion deposit were observed on fracture surfaces tested in air at low R values where growth rates had been less than 10^{-7} mm/cycle (i.e. near ΔK_o). Such bands were not observed at high R values, and were far less pronounced in hydrogen gas.

With increasing growth rates above ΔK_o, the influence of hydrogen gas becomes progressively lessened. However, around 10^{-5} mm/cycle (at $R < 0.5$), a second enhancement in growth rates due to hydrogen (up to 20 times) can be observed in the form of an abrupt acceleration in hydrogen-assisted growth (Fig. 8-10) similar to that observed in 300-M (Fig. 7), which is both sensitive to frequency and load ratio. Provided the frequency is below a critical value (dependent upon R), the onset of the acceleration occurs at a constant maximum stress intensity K_T^{max} of approximately 20 MPa$\sqrt{m}$, i.e. at lower ΔK levels with increasing load ratios (Table II and Fig. 9). Further, growth rates in hydrogen above K_T^{max} were increased with decreasing frequency, whilst rates in air above 10^{-5} mm/cycle were largely insensitive to both frequency and load ratio. Unlike near-threshold behavior, a characteristic fracture mode for hydrogen-assisted cracking was observed; failures were predominately transgranular in air and in hydrogen below K_{max}^T, and predominately intergranular in hydrogen above K_{max}^T where an acceleration had occurred (Fig. 13). This effect of hydrogen on higher growth rates, with its characteristic fracture mode and frequency/load ratio dependence, appears very similar to the stress-corrosion fatigue[30] observed in high strength steels, with the very notable exception that in these low strength steels the onset of this effect occurs at K_{max}^T values far below the sustained-load K_{Iscc} threshold.

Summarizing, data obtained on lower strength 2¼Cr-1Mo bainitic steel indicate that marked hydrogen-assisted crack propagation occurs both at near-threshold levels and at higher growth rates at stress intensities well below K_{Iscc}. Thus, for a steel generally considered to be relatively immune to hydrogen embrittlement (under sustained loads), it is clear that the presence of dry hydrogen gas results in a significant reduction in ΔK_o, in addition to accelerating growth rates by up to two order of magnitude.

4. DISCUSSION

Although there have been many mechanisms for hydrogen embrittlement proposed over the years, such as the Pfeil-Troiano-Oriani decohesion models[33] and the Zappfe pressure model[34], no single theory gives a complete description to the problem. For high strength steels, however, in "hydrogen-producing" atmospheres, e.g. H_2, H_2S, H_2O, etc., under both monotonic and cyclic loading, decohesion theories are now quite widely accepted[26-29,33]. Hydrogen-assisted failure in lower strength ductile steels, on the other hand, is still poorly understood, and few mechanistic studies have been performed for such failure under cyclic loading. No studies have been reported for the problem of hydrogen-assisted failure at near-threshold stresses.

Through examination of a very wide range of growth rates (six decades) in both low strength and high strength steels, the present work indicates that there are two distinct growth rate regimes where gaseous hydrogen can markedly enhance crack propagation rates with respect to air, i) at near-threshold levels at low load ratios, and ii) at higher growth rates above a critical K_{max} value (K^T_{max}). Significant differences in behavior, however, exist between low and high strength steels. We now examine each regime in turn. (It should be appreciated that the treatment given and the models proposed are, at this stage, far from complete but it is felt that they provide a good framework for future investigation).

1) Higher Growth Rate Regime.

Both high and low strength steels show an abrupt onset of hydrogen-assisted fatigue fracture at higher growth rates above a critical K_{max} value (K^T_{max}). The environmentally-enhanced propagation is coincident with a change in fracture mode from predominately transgranular to predominately intergranular cracking in the lower strength steel and is promoted by decreasing frequency. In high strength 300-M steel, this transition occurs when $K^T_{max} \approx K_{Iscc}$, whereas in lower strength SA542-3 the effect of hydrogen is observed at K_{max} values far below K_{Iscc}.

Several authors have observed marked hydrogen-assisted growth in high strength steels when K_{max} exceeds K_{Iscc}[27,28,30]. The phenomenon, which is often referred to as stress-corrosion fatigue[30], has been usefully rationalized in terms of "superposition"[27] or "process-competition"[28] models, where the environmentally-assisted crack propagation is considered to be simply a result of sustained-load stress-corrosion cracking and mechanical fatigue components which are either additive or mutually competitive. Careful reaction kinetic studies have revealed that such cracking is rate-limited by surface reactions at the crack tip, namely chemisorption of hydrogen atoms for gaseous hydrogen atmospheres and oxidation of the iron surface for water environments[31,35].

The current studies show that analogous effects may occur in low strength steels, but at stress intensities below K_{Iscc}, i.e. where no such hydrogen-assisted cracking would take place under sustained loading. The onset of "apparent" stress-corrosion fatigue in low strength steels below K_{Iscc} may be considered to result from the fact that cyclic loading will maintain a sharp crack tip and thus continuously provide freshly exposed metal surface there for hydrogen to adsorb[32]. Further, in such strain-rate sensitive, ductile steels, the K_{Iscc} environmental threshold cannot be taken as a material constant for a particular alloy/environmental system, and can be expected to be reduced under dynamic (i.e. cyclic) straining conditions[36]. This implies that the environmental contribution to crack growth $(da/dt)_{env}$, defined in terms of the difference between the crack growth increment per unit time in hydrogen and in the reference inert atmosphere, i.e.

$$\left(\frac{da}{dt}\right)_{env} = \left[\left(\frac{da}{dN}\right)_{H_2} - \left(\frac{da}{dN}\right)_{air}\right]\nu \quad , \qquad (3)$$

whould be <u>increased</u> with <u>increasing</u> frequency (ν), consistent with current observations (Fig. 14). The environmental component can be seen to fall off at low frequencies as behavior under static load conditions is approached. Similar results have been reported for lower strength steels in aqueous environments[37,38], and may be consistent with a strain-rate dependence of hydrogen transport within the metal lattice. Such a dependence is feasible if the hydrogen transport mechanism is via Cottrell atmospheres on mobile dislocations ("dislocation sweep-in-mechanism"[25]). Hydrogen permeation measurements on plastically-deformed samples as a function of strain rate were instigated in this program to examine this effect.

ii) Near-Threshold Regime.

The most pronounced influence of gaseous hydrogen in accelerating crack propagation rates was seen at near-threshold levels, below 10^{-6} mm/cycle, but surprisingly only at low load ratios in lower strength SA542-3 steel without apparent change in fracture mechanism. Near-threshold growth in ultrahigh strength 300-M steel, which is markedly more prone to hydrogen embrittlement, was not accelerated in the presence of dry hydrogen gas. These results are somewhat at variance with the concept[4] proposed previously that mechanical and microstructural factors which are known to affect near-threshold behavior, e.g. strength level, mean stress, etc. can be rationalized in terms of environmental effects and, in particular, hydrogen embrittlement mechanisms for steels. While it is obviously premature to completely rule out hydrogen embrittlement mechanisms at this stage, an alternative explanation is warranted. It is tentatively suggested that the large acceleration due to gaseous hydrogen in low strength steels at low R ratios may not be entirely associated with hydrogen embrittlement *per se*, but instead involve a phenomenon which we term "fretting-oxide-induced" crack closure.

At low load ratios, typically below $R = 0.5$, as a result of residual plastic deformation left in the wake of a growing fatigue crack, some closure of the crack surfaces occurs at positive loads during the loading cycle. This is known simply as crack closure, or more correctly in our terminology "plasticity-induced crack closure". Since the crack is unable to propagate whilst it remains closed, the net effect of closure is to reduce the applied ΔK value (computed from applied load and crack length measurements) to some lower effective value (ΔK_{eff}) actually experienced at the crack tip. As mean stress (or load ratio) is increased, the crack remain open for a larger portion of the cycle thereby increasing ΔK_{eff}, until above a load ratio of roughly 0.5, the crack remains open during the entire cycle and $\Delta K_{eff} = \Delta K_{applied}$. It has been appreciated for some time that the amount of crack closure may be more significant at near-threshold levels[12] (this incidently may explain the large load ratio effect on ΔK_o), yet no sensible explanation for this has been proposed.

Now, we examine the effect of this plasticity-induced crack closure on a near-threshold crack propagating in a moist environment such as air. Once fresh reactive surface is created at the crack tip it will readily oxidize. Measurements of the thickness of the oxide layer indicate that the thickness is i) inversely proportional to local crack growth rate and ii) two to three times thicker* than that which forms by simple exposure of the metal for the same time in the same environment[39]. A mechanism for this enlarged oxide deposit at very low growth rates can be thought of as "fretting oxidation"[39,40]. Plasticity-induced closure causes contact between the two fracture surfaces, and the associated tangential friction between the crack walls may lead to local re-welding of fresh surface with subsequent decohesion in different locations, and cracking in the naturally formed oxide scale. The result is to generate new zones of fresh surface, further oxidation, and a thickening of the oxide film. At high load ratios, however, where there is little plasticity-induced crack closure to cause contact between surfaces, such fretting oxidation will not occur, consistent with observations of visible bands of corrosion deposits on near-threshold fracture surfaces at low R, and their absence at high R[2,39,41] (Fig. 15).

The significance of this excess oxide debris is that it will generate increased crack closure, because, although its presence will "wedge-open" the crack, on the closing portion of the load cycle, contact between the two fracture surfaces will occur earlier, thereby increasing closure loads and thus decreasing ΔK_{eff}. The effect of this "fretting-oxide-induced" crack closure at near-threshold levels can be appreciated by realizing that typical oxide films can be of the order of several microns in near-threshold cracks where predicted crack tip opening displacements** are less than 0.2 μm. In dehumidified*** environments such as gaseous hydrogen, however, the amount of oxidation is reduced to negligible proportions, such that there is no mechanism for increased (oxide-induced) crack closure and ΔK_{eff} remains unchanged. We are thus proposing that the marked influence of hydrogen in accelerating <u>near-threshold</u> growth rates and lowering threshold ΔK_o values in low strength steels may be simply due to the fact that the environment is dry or oxygen free. In moist air, oxide-induced closure will decrease ΔK_{eff} resulting in lower growth rates and higher ΔK_o values. At high load ratios (i.e. R = 0.75), however, such a mechanism cannot occur since there is no plasticity-induced closure. Thus we would expect no difference between air and

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*typically up to several microns

**Maximum crack tip opening displacements computed from 0.49 $K_{max}^2/2\sigma_y E$.

***We are uncertain at this stage whether it is the lack of oxygen, or moisture, or both that reduces fretting oxidation.

hydrogen environments at high R, consistent with the fact that little oxide deposit is seen and that threshold values and subsequent growth rates are almost identical (Fig. 11). The fact that hydrogen has little influence on threshold behavior in high strength steels (see Fig. 6) can also be rationalized in terms of this model, since (plasticity-induced) crack closure is much reduced in high strength materials and further, an oxide particle on the harder fracture surface is capable of doing less fretting damage. Such an explanation may account for the fact that the large effect of strength level on ΔK_o values is seen only at lower load ratios; at R values approaching 0.7-0.8 near-threshold growth rates are largely insensitive strength level[3]. Moreover, the concept of oxide-induced closure readily provides a mechanism for the fact that closure is more significant at lower growth rates, and is consistent with observations that near-threshold fracture surfaces are generally "fuzzy" and difficult to image sharply in scanning electron micrographs[40,42]. The model is also consistent with the fact that there is no change in fracture mechanism near ΔK_o between hydrogen and air environments (Fig. 12), despite the large acceleration due to the presence of hydrogen, and further it removes the difficulty of explaining why hydrogen accelerates growth above K^T_{max} values, but not at lower stress intensities until ΔK_o is approached.

It is to be appreciated that this model is in its infancy and many details and critical experiments remain to be worked out. Such experiments include testing in wet, dry, and oxygen-free environments, interrupted tests where hydrogen is suddenly replaced by air and vice versa, measurement of apparent activation energies for near-threshold crack growth, measurement of oxide scale thickness as a function of crack velocity and examination of the effect of vacuum. Many of these tests are planned for the coming year. We are encouraged though by our initial critical experiments of testing in inert gas, in this case dehumidified gaseous argon. The results (Fig. 16), which incidentally are for normalized 2¼Cr-1Mo steel, indicate that the threshold in dry argon is almost identical to that in dry hydrogen, and below that in moist air, i.e. dry argon accelerates near-threshold growth rates relative to air. The fact that dry argon behaves like dry hydrogen is clearly inconsistent with any hydrogen embrittlement mechanism, yet is totally in accord with the concept of oxide-induced closure.

Several hitherto unexplained observations in the literature are also now capable of interpretation in terms of this model. For example, Amzallag[18] reports lower thresholds in argon gas relative to air for 316 stainless steel. Similarly, results in A533B[14] and a NiCrMoV rotor steel[13] show slightly higher ΔK_o values in water compared to air. Tu and Seth[17] actually mention the presence of corrosion products forming at the crack tip in their paper describing observations of higher thresholds in steam relative to air at elevated temperatures for a range of steels.

Thus it is concluded that the influence of gaseous hydrogen on fatigue crack propagation in steels may result from two very different physical phenomena. At higher growth rates above a critical K_{max} value, the enhancement in crack velocity due to hydrogen appears to be associated with hydrogen embrittlement, although precise mechanisms of embrittlement in low strength steels remain to be determined. The limiting K_{max} value for this effect or effective threshold for corrosion fatigue, K^T_{max}, is nominally equal to the sustained-load stress-corrosion threshold, K_{Iscc}, in strain-rate insensitive, high srength steels, whereas it is much less than K_{Iscc} in lower strength steels, possibly due to an influence of strain rate on K_{Iscc} from hydrogen transport limitations. At near-threshold growth rates, however, it is our contention that the marked acceleration in crack velocity due to hydrogen results more from the absence of moisture (and/or oxygen) in limiting "fretting-oxide-induced crack closure" than any embrittlement mechanism *per se*. We plan to develop these concepts fully in the coming program year.

Finally, it is worth mentioning that, if substantiated, the possible ramifications of these effects are extremely important. First, susceptability to stress corrosion cracking of lower strength steels in gaseous hydrogen should not be assessed merely on the basis of sustained load data, such as K_{Iscc} values, since significant hydrogen-assisted subcritical crack propagation can occur at stress intensities far less than K_{Iscc} in the presence of cyclically varying loads. This is in agreement with the work of Ford[36] and Wei[31]. Second, the potential problem of hydrogen embrittlement in natural gas pipelines during their proposed usage for energy transportation by gaseous hydrogen must be carefully considered. At first glance, the use of SA516 or X-65 low strength steels for such pipelines would suggest that there is no problem since such steels are considered to be relatively immune to gaseous hydrogen embrittlement, based on sustained load K_{Iscc} data. However, since hydrogen pipelines will contain in-line compressors, clearly cyclic loading will be present, and in view of the typical hoop stresses and flaw sizes involved, conditions are likely to be in the near-threshold regime[43]. Although such data are presently being generated[43], it is probable that hydrogen will give rise to a marked enhancement in near-threshold crack velocities very similar to that observed in 2¼Cr-1Mo steel. However, if oxide-induced closure arguments are correct, this potentially damaging "embrittlement" may simply be reduced by introducing into the gas stream traces of moisture and/or oxygen. Traces of oxygen, of course, have additional advantages since selective adsorption of oxygen atoms at the crack tip can markedly reduce susceptibility to "true" hydrogen embrittlement as well.

5. CONCLUSIONS

Based on a study of the characteristics of low-growth rate fatigue crack propagation in ultrahigh strength 300-M and lower strength 2¼Cr-1Mo steels, tested in moist air, dry gaseous argon and dry gaseous hydrogen environments, the following general conclusions can be made:

1) There are two distinct growth rate regimes where fatigue crack propagation rates in gaseous hydrogen may be considerably enhanced compared to air, namely at near-threshold levels below 5×10^{-6} mm/cycle, and at higher growth rates usually exceeding 10^{-5} mm/cycle.

2) The influence of hydrogen at higher growth rates occurs in both high and low strength steels above a critical stress intensity K^T_{max}. K^T_{max} values are nominally equal to K_{Iscc} in 300-M, and far below K_{Iscc} in SA542-3.

3) Based on data primarily on SA542-3, hydrogen-assisted crack propagation at such higher growth rates is enhanced by decreasing frequency and increasing load ratio, and involves a fracture mode change from predominately transgranular to predominately intergranular.

4) Hydrogen-assisted crack propagation at higher growth rates is ascribed to some mechanism of hydrogen embrittlement, presumably involving

decohesion at grain boundaries in SA542-3. Behavior is analogous to so-called "stress-corrosion fatigue".

5) At near-threshold levels, hydrogen-assisted growth is observed only in low strength steels at low load ratios, and involves no apparent change in fracture mechanism with respect to moist air. No influence of hydrogen is observed near ΔK_o for 300-M or for SA542-3 at R = 0.75.

6) On near-threshold fracture surface, corrosion debris may be formed where growth rates were less than 10^{-7}mm/cycle. Little or no corrosion deposites are seen at high load ratios or in high strength steels, and deposits are less for tests in hydrogen gas.

7) Hydrogen embrittlement mechanisms for the influence of gaseous hydrogen on near-threshold behavior are questioned since near-threshold growth rates in dry gaseous argon are similar to hydrogen, and are accelerated with respect to air. In addition, ΔK_o values in argon are similar to those measured in hydrogen, and are <u>lower</u> than ΔK_o values measured in air.

8) The influence of dry gaseous hydrogen (and argon) on near-threshold fatigue crack growth behavior is ascribed to a new mechanism involving fretting-oxide-induced crack closure. Accordingly to this model, near-threshold growth rates are accelerated in hydrogen because the environment contains less moisture (and/or oxygen) compared to air. Moist environments result in oxide films formed at the crack tip, which are thickened by fretting oxidation arising from plasticity-induced crack closure. The enlarged oxide debris within the crack can then lead to increased closure thereby reducing effective ΔK values at the crack tip. Such models appear consistent with experimental data.

6. PERSONNEL

The work performed in the program is under the direction of Professor Robert O. Ritchie of the Department of Mechanical Engineering, Massachusetts Institute of Technology. The personnel involved in the program and their specific projects are listed below:

a) Current personnel:

i) Prof. R. O. Ritchie, principal investigator

ii) S. Suresh, research assistant
iii) J. Toplosky, research assistant
iv) H. Conley, undergraduate.

b) Current projects:

i) "Influence of Gaseous Environments on Fatigue Crack Propagation in a Bainitic $2\frac{1}{4}$Cr-1Mo Pressure Vessel Steel"
S. Suresh, Ph.D. thesis, expected 1981.

ii) "Hydrogen-Assisted Fatigue Crack Propagation in Ultrahigh Strength 300-M Steel",
J. Toplosky, S.M. thesis, expected 1980.

iii) Relationship between Hydrogen-Assisted Cracking under Sustained and Cyclic Loads in Ultrahigh Strength Steel",
H. Conley, S.B. thesis, January 1980.

c) Publications:

S. Suresh, C. M. Moss, and R. O. Ritchie: "Hydrogen-Assisted Fatigue Crack Growth in $2\frac{1}{4}$Cr-1Mo Low Strength Steels", Proceedings of the Second International Japan Institute of Metals Symposium on Hydrogen (JIMIS-2), Minakami Spa, Japan, 1979 (Japan Institute of Metals, Sendai, Japan, 1980).

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Thanks are due to Drs. John Landes and Don McCabe of Westinghouse R&D Center, Pittsburgh, for supplying the thick-section plates of $2\frac{1}{4}$Cr-1Mo steel, to Professor R. M. Latanision and Mr. M. Kurkels for use of the hydrogen permeation equipment, and to Dr. T. C. Lindley for helpful discussions.

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Table I

Chemical Composition in Weight Percent of Steels Investigated

	C	Mn	Si	Ni	Cr	Mo	Cu	P	S	V
300-M	0.42	0.76	1.59	1.76	0.76	0.41	-	0.007	0.002	0.10
SA542-3	0.12	0.42	0.25	0.14	2.48	1.06	0.16	0.013	0.020	-

Table II

Ambient Temperature Mechanical Properties of Steels Investigated

Steel	Condition	0.2% Proof Stress	U.T.S.	% elong.	Charpy Impact Energy	K_{Ic}	K_{Iscc}[1]
		(MPa)	(MPa)		(J)	(MPa$\sqrt{m}$)	(MPa$\sqrt{m}$)
300-M	T300	1737	2006	12[2]	25	65	33
300-M	T650	1074	1186	18[2]	55	152	-
SA542-3	¼T-½T	500	610	25[3]	200	295	85

[1] For ambient temperature gaseous hydrogen (atmospheric pressure)

[2] On 25 mm gauge length

[3] On 45 mm gauge length

Table III

Conditions for Onset of Hydrogen-Assisted Crack Growth in SA542-3

R	Frequency (Hz)	ΔK^T (MPa$\sqrt{m}$)	K^T_{max} (MPa$\sqrt{m}$)
0.05	50	no effect	
0.05	5	no effect	
0.05	2	21.8	22.9
0.05	0.5	21.2	22.3
0.30	50	15.3	21.9
0.30	5	14.4	20.6
0.50	50	11.8	23.6
0.75	50	4.7	18.8

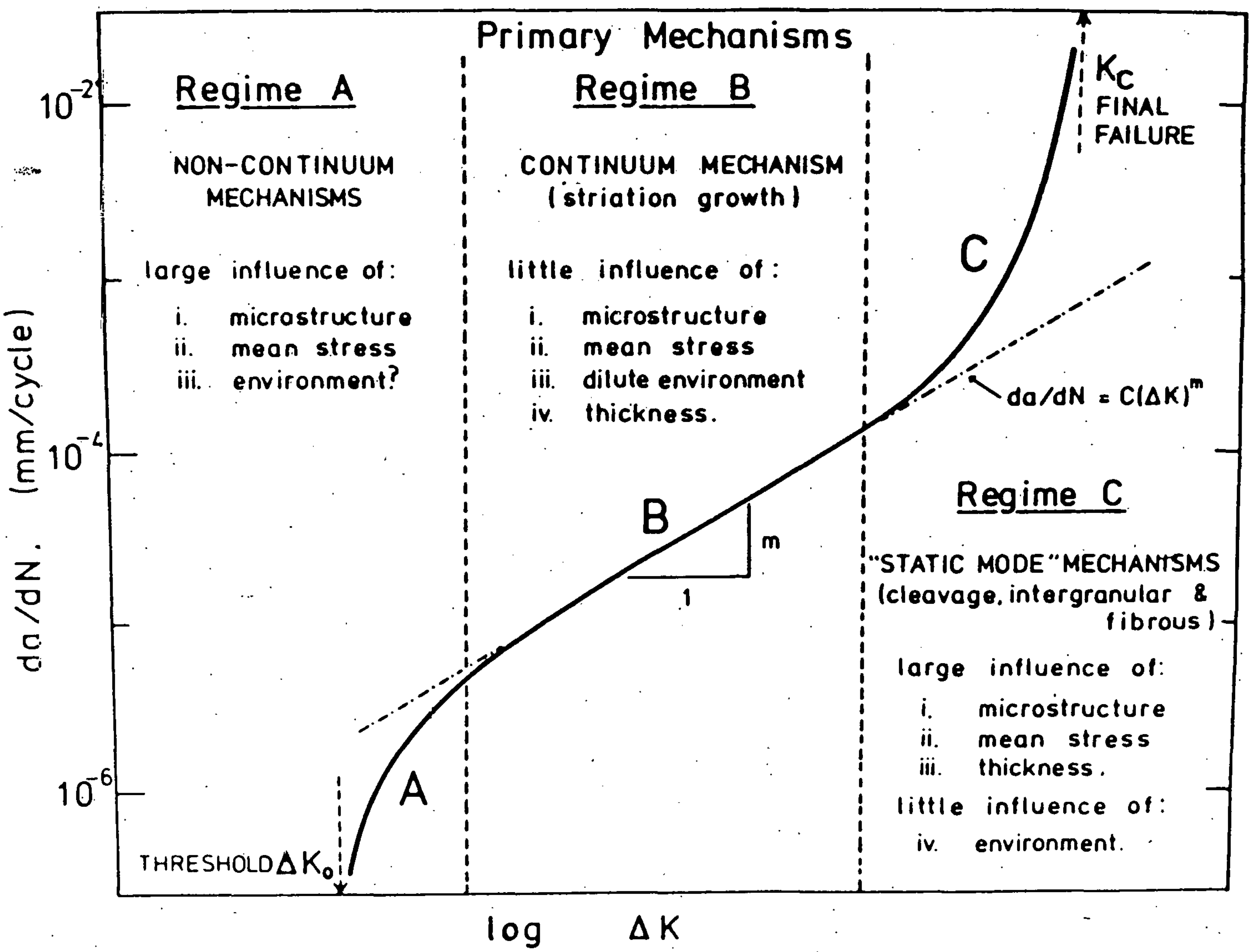

Fig. 1 Schematic variation of fatigue crack growth rate (da/dN) with alternating stress intensity (ΔK) in steels, showing primary crack growth mechanisms. ΔK_o is the threshold stress intensity, K_c is the stress intensity at final failure.

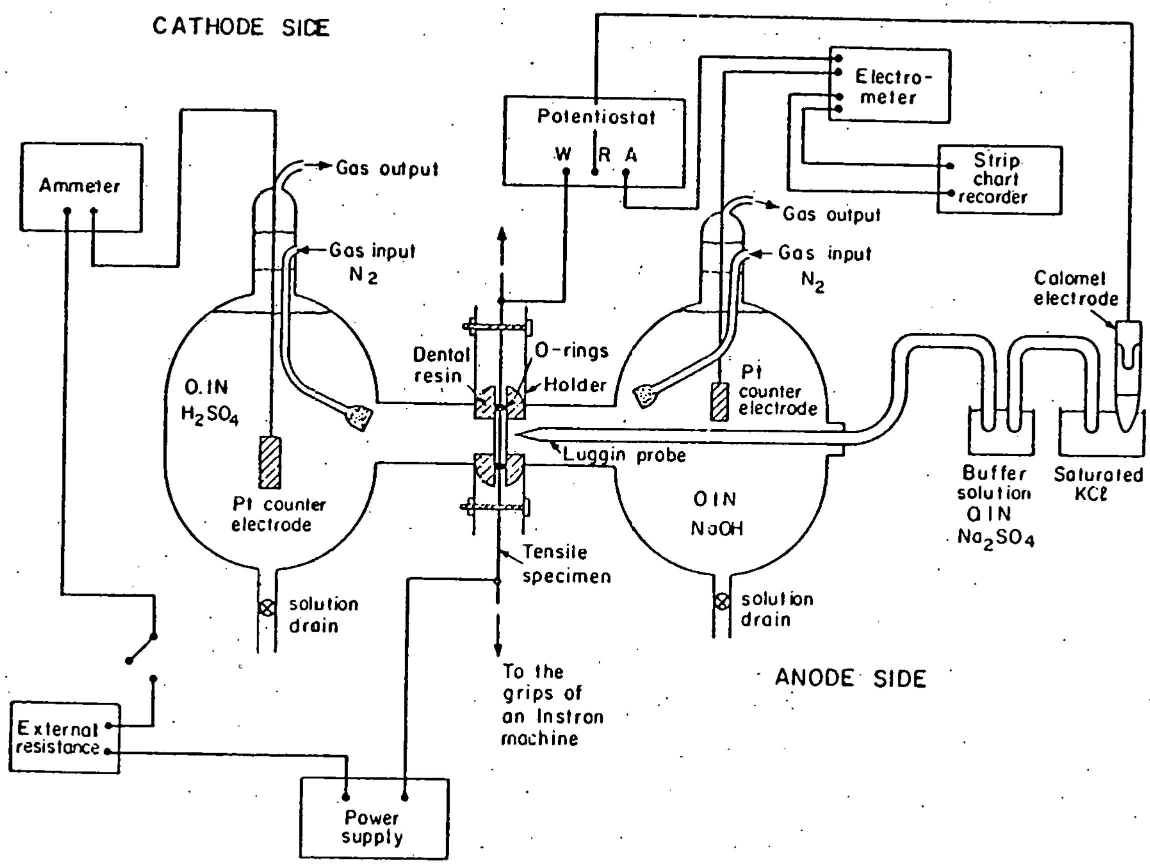

Fig. 2: HYDROGEN PERMEATION CELL

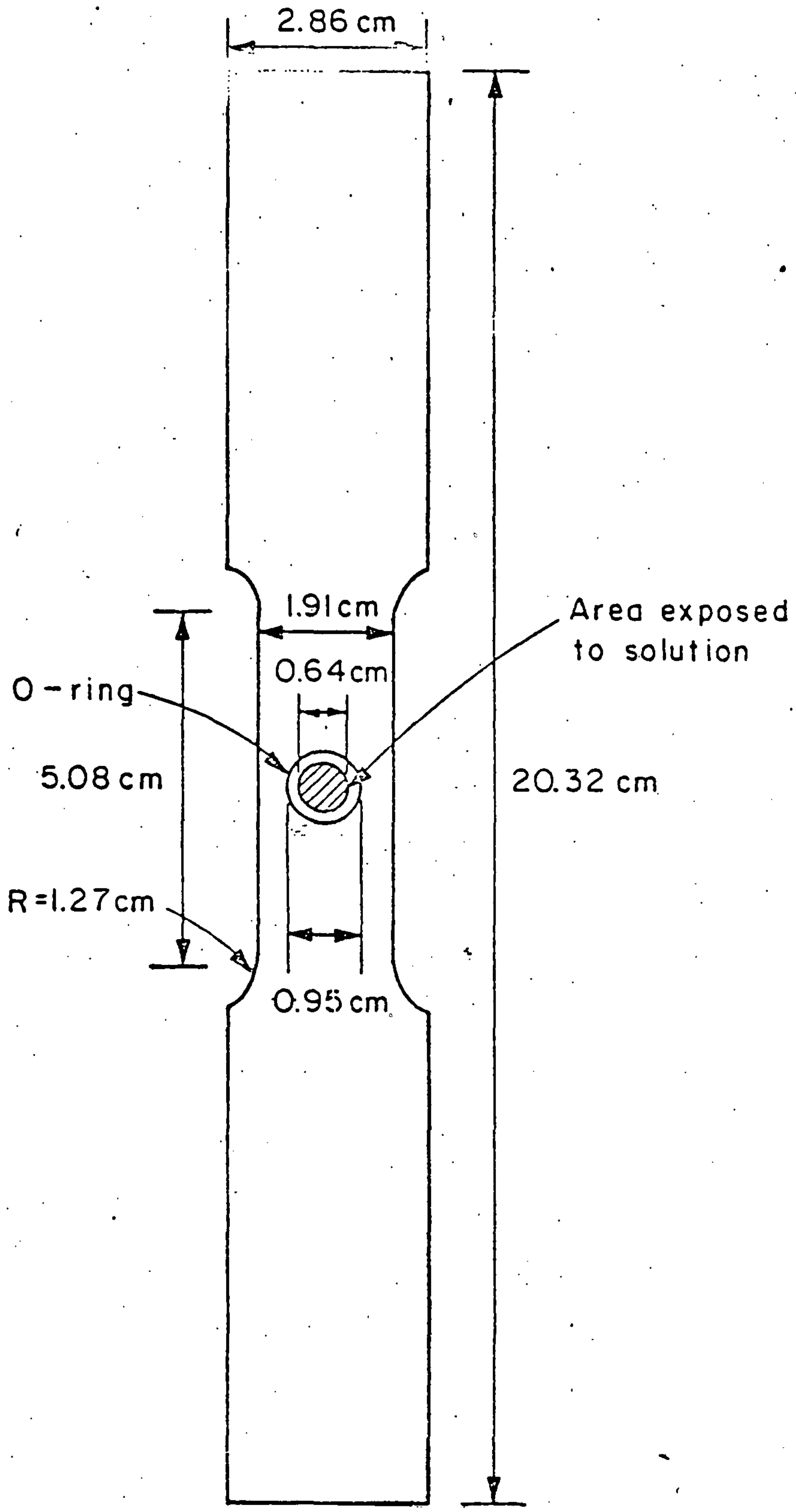

Fig. 3: Dimensions of specimen for permeation experiment under plastic deformation

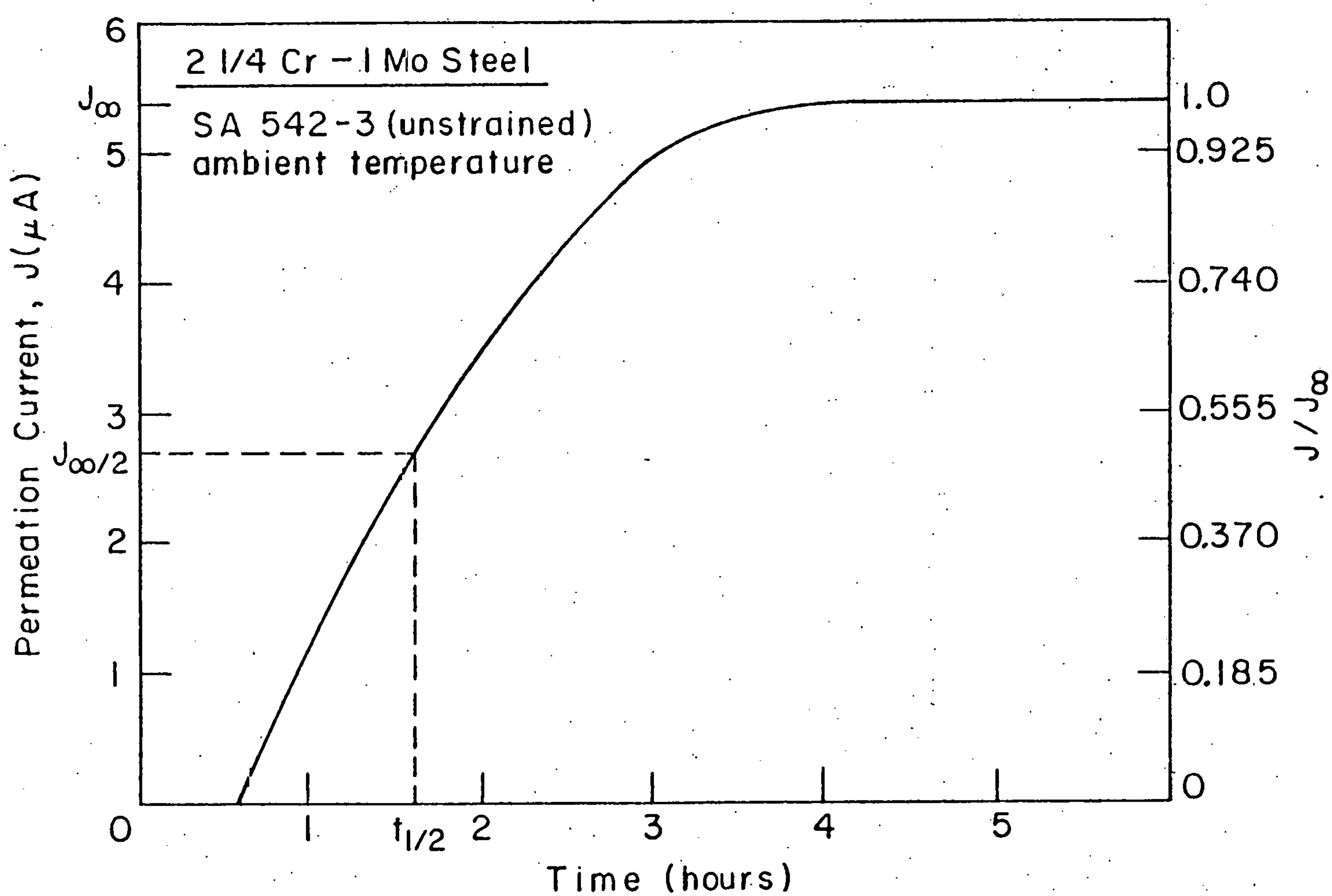

Fig. 4: Variation of permeation current with time for unstrained specimen of SA542-3.

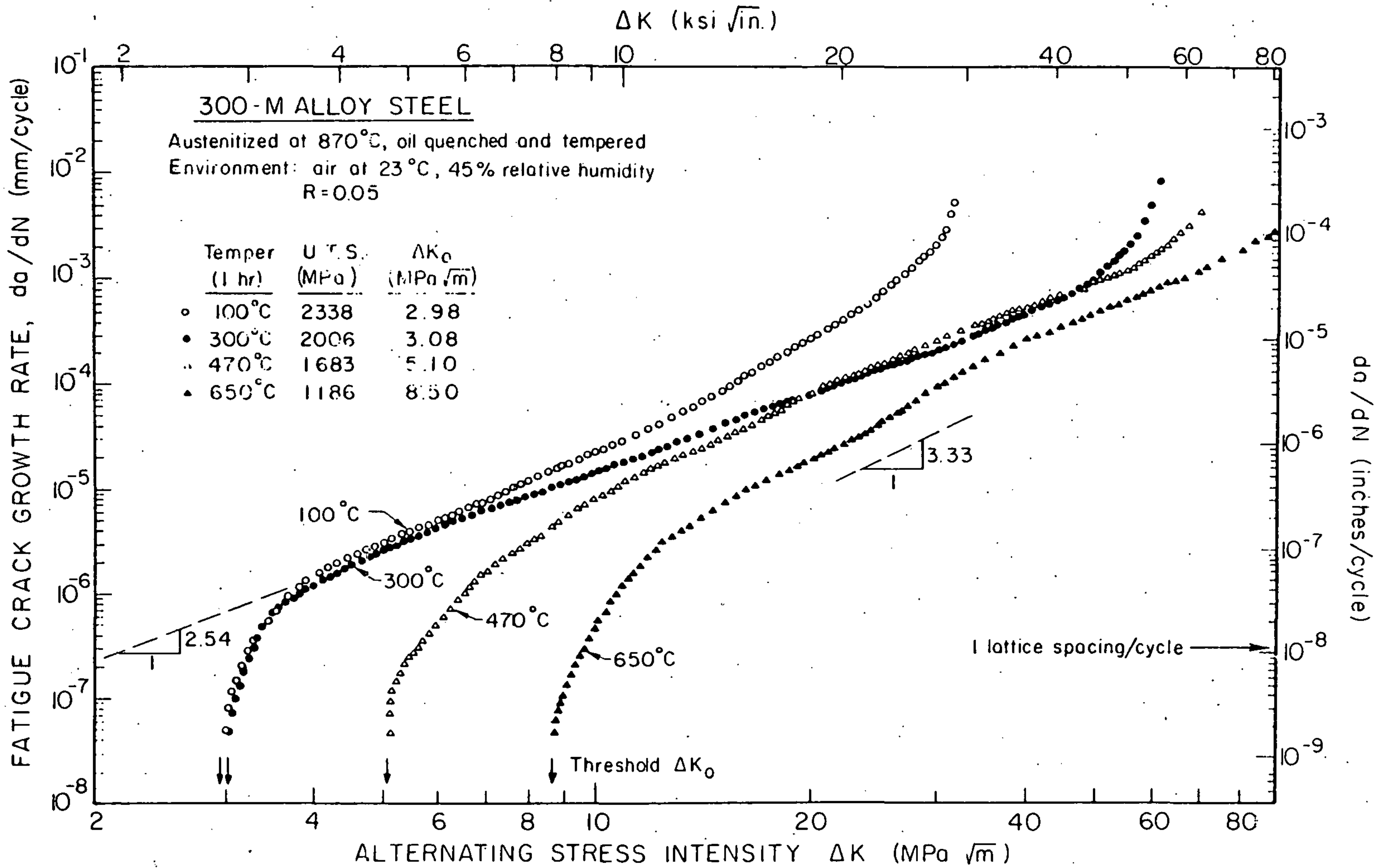

Fig. 5: Variation of fatigue crack propagation (da/dN) with alternating stress intensity (ΔK) for 300-M ultrahigh strength steel, quenched and tempered at 100, 300, 470 and 650°C. Tests at R = 0.05 in ambient temperature moist air at 50 Hz (after Ritchie[3]).

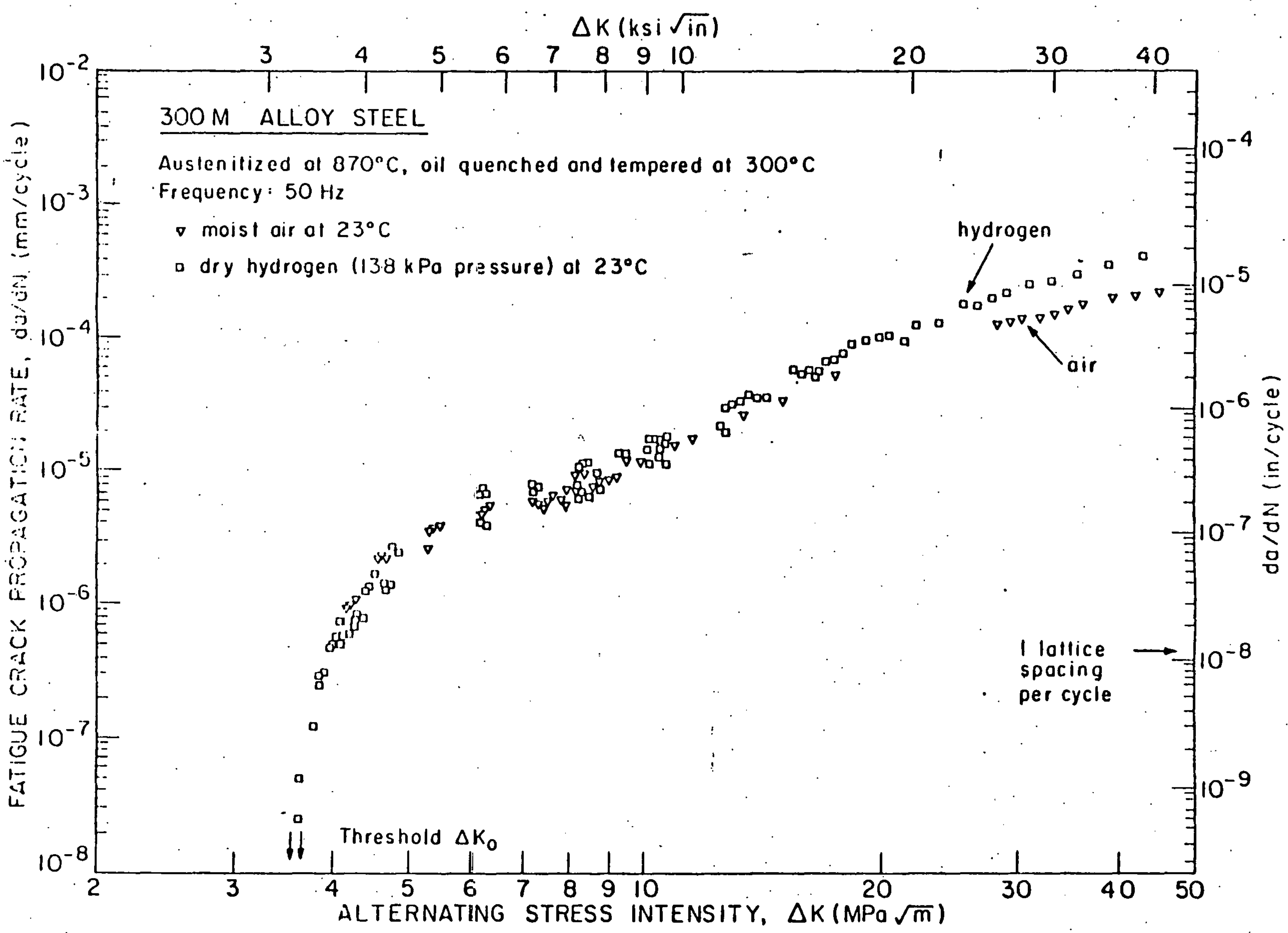

Fig. 6; Fatigue crack growth data for 300-M, tempered at 300°C, in moist air and dry hydrogen gas.

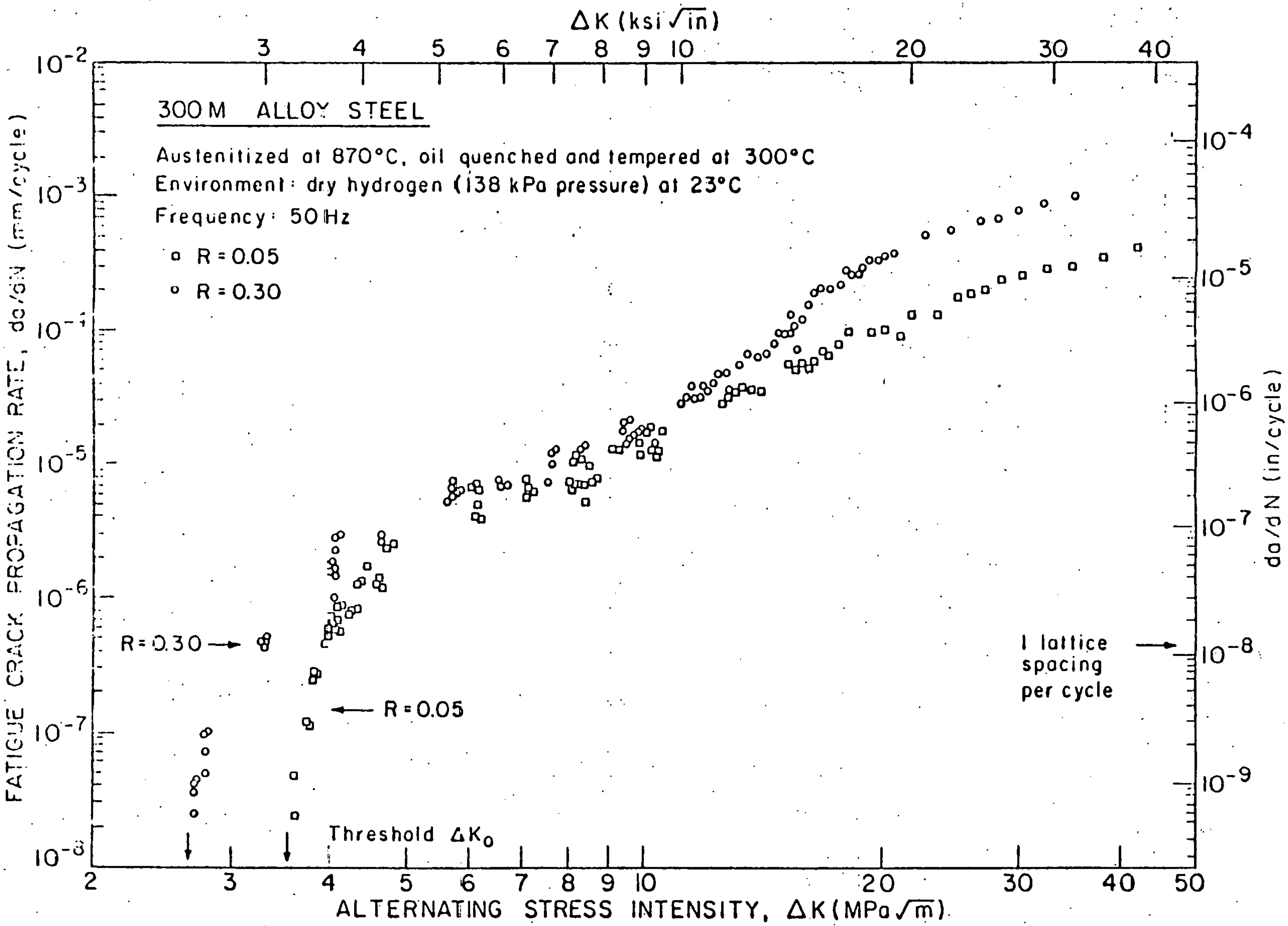

Fig. 7; Influence of load ratio R on fatigue crack growth in 300-M, tempered at 300°C, tested at 50 Hz in dry hydrogen gas.

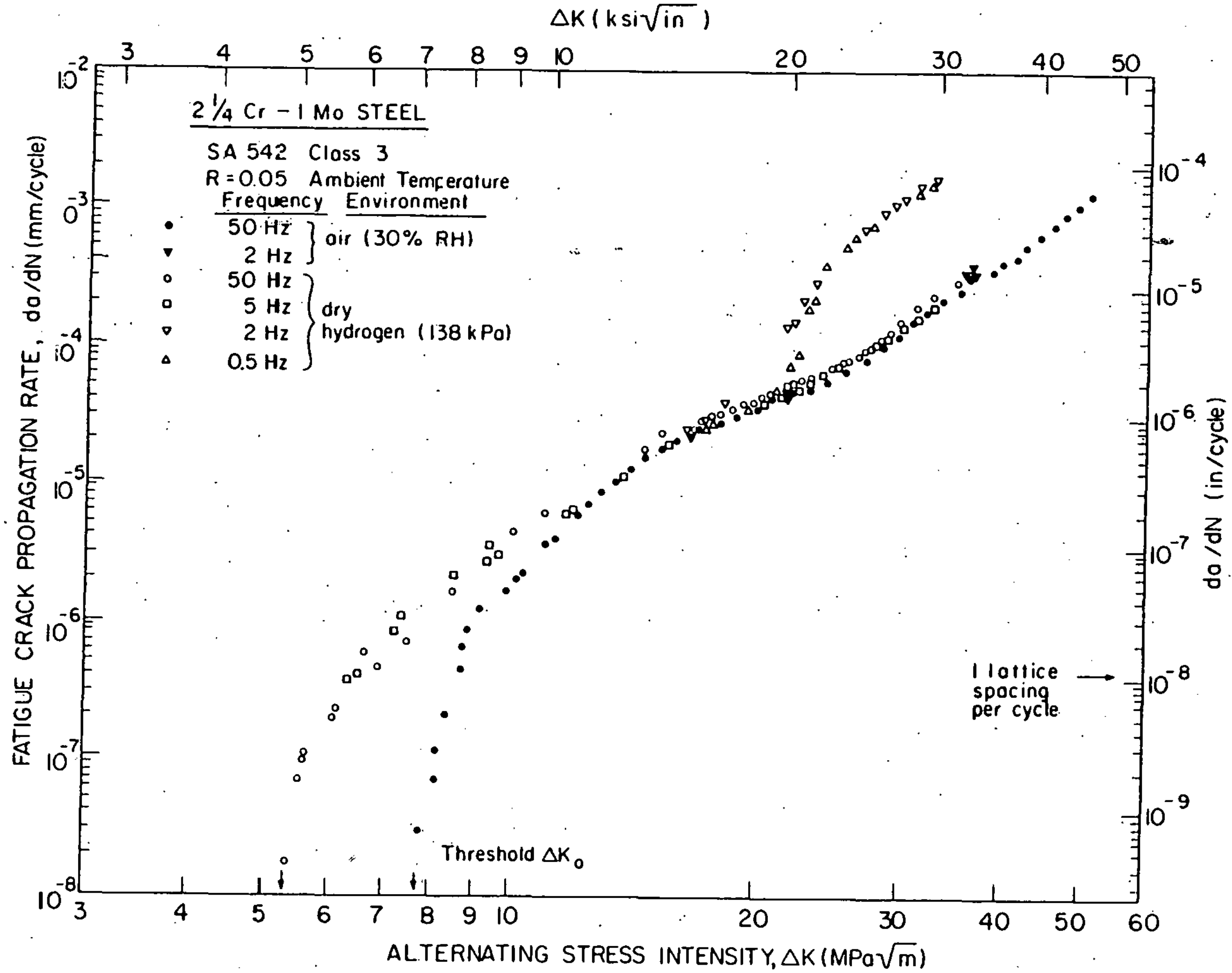

Fig. 8: Influence of frequency on fatigue crack growth in SA542-3, tested at $R = 0.05$ in moist air and dry hydrogen.

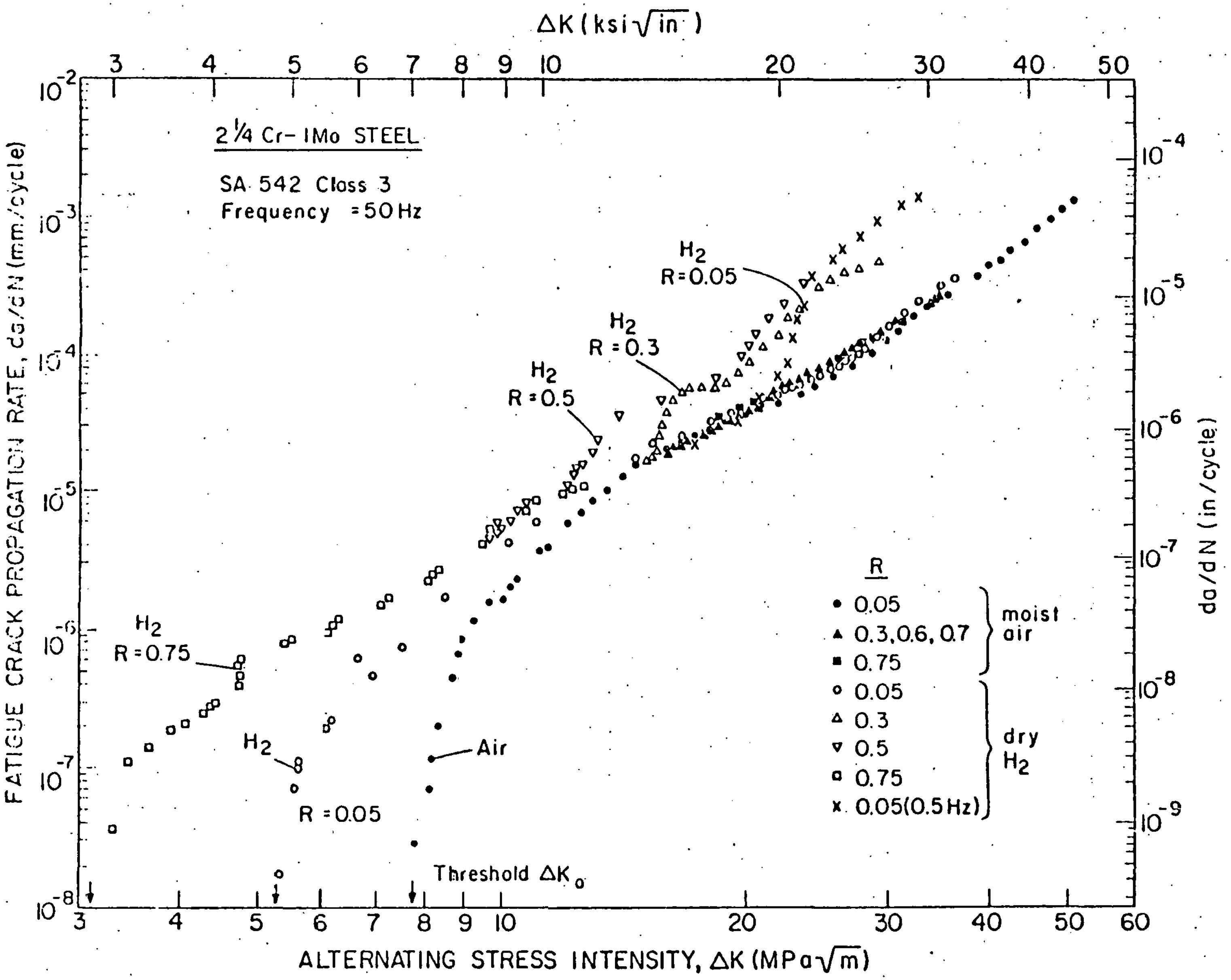

Fig. 9: Influence of load ratio R on fatigue crack growth in SA542-3, tested at 50 Hz in moist air and dry hydrogen.

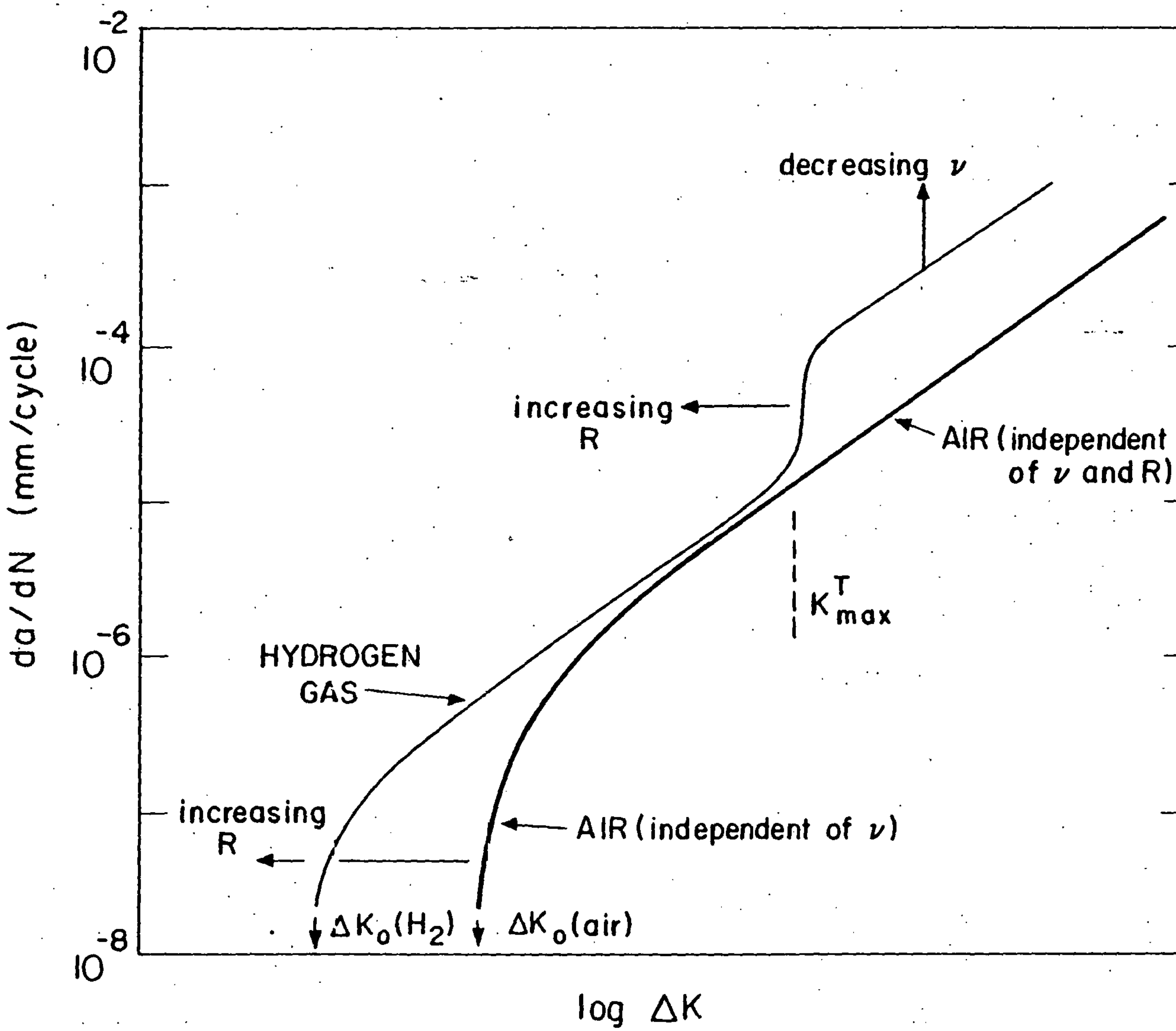

Fig. 10: Schematic diagram showing regimes of hydrogen-assisted growth for lower strength steels.

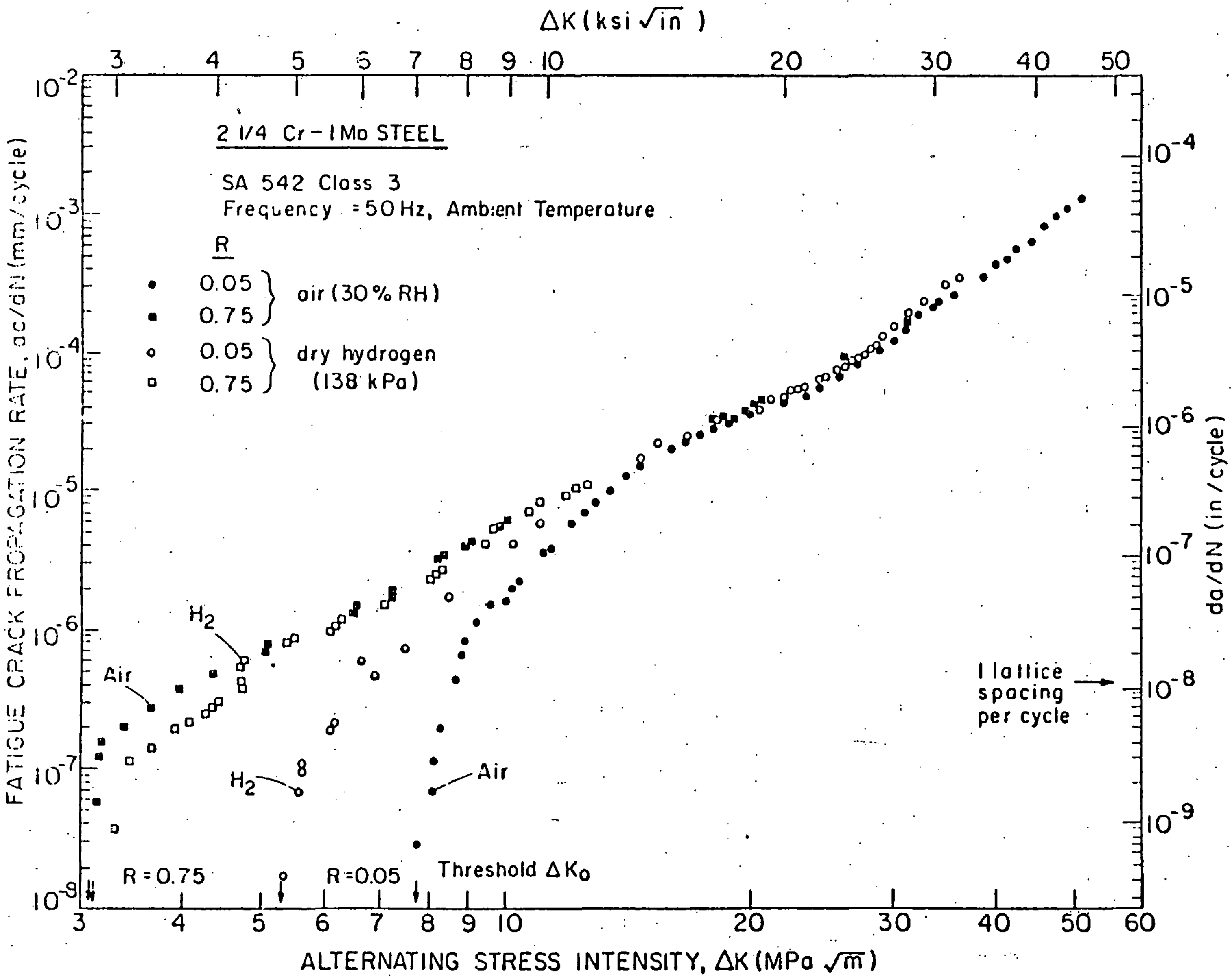

Fig. 11: Fatigue crack growth data for SA542-3 at R=0.05 and 0.75 in moist air and dry hydrogen at 50 Hz, showing marked influence of hydrogen gas on near-threshold growth rates only at low load ratios.

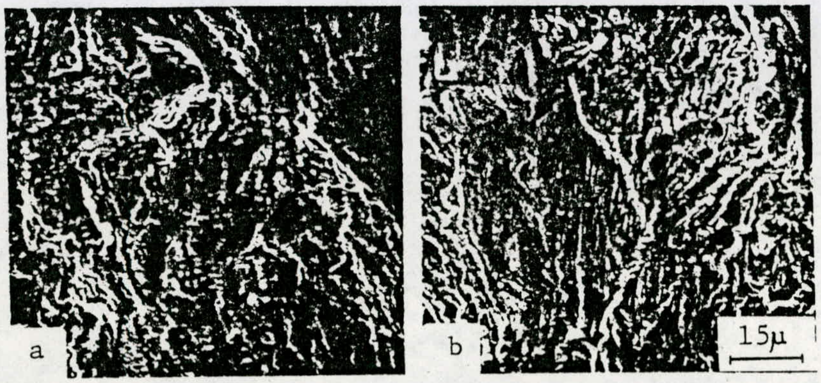

Fig. 12: Mechanisms of near-threshold fatigue crack growth in 2¼Cr-1Mo steel at 50 Hz, a) in moist air and $\Delta K = 9.2\ MPa\sqrt{m}$, b) in dry hydrogen at $\Delta K = 7.2\ MPa\sqrt{m}$ ($R = 0.05$).

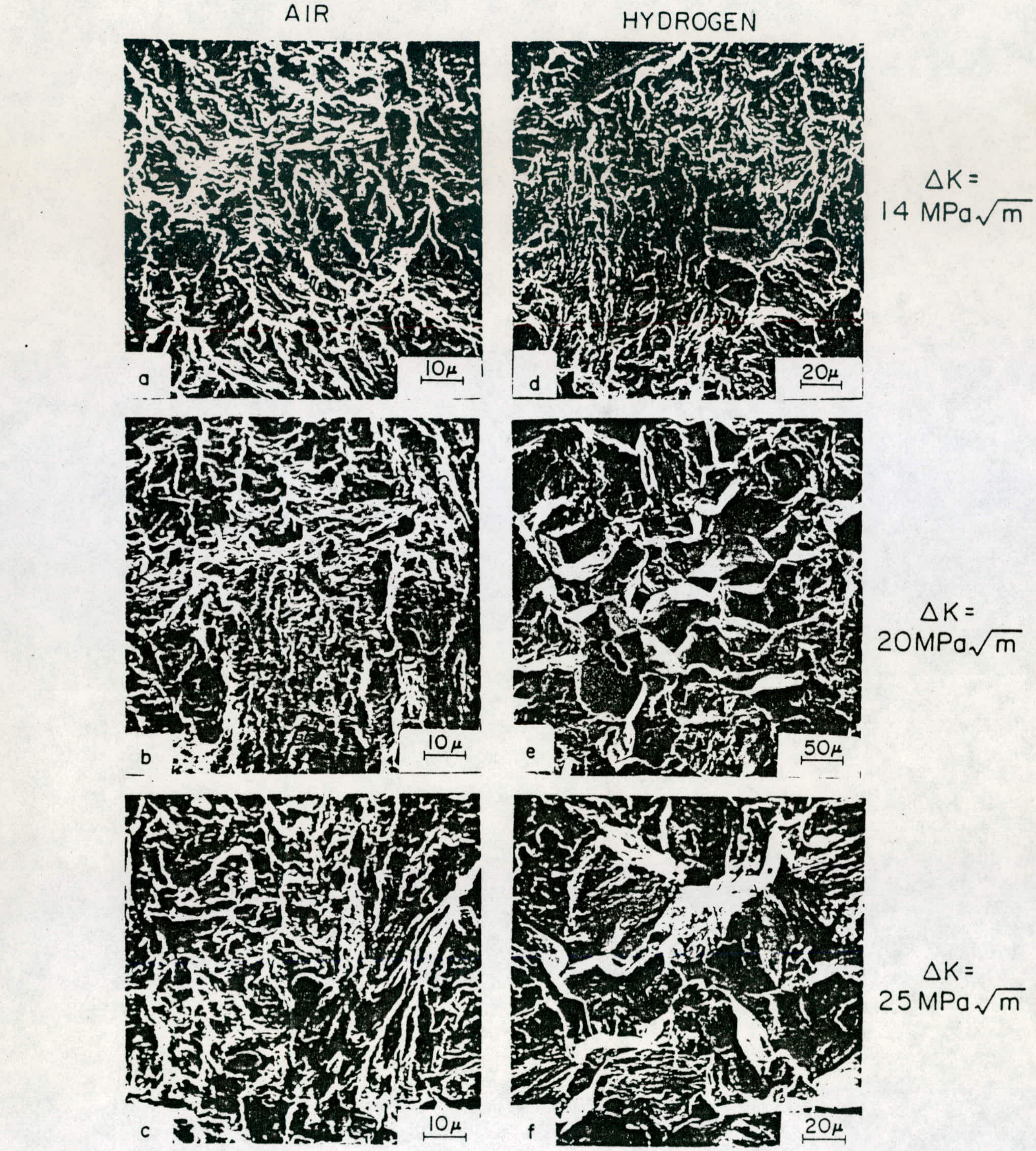

Fig. 13: Mechanisms of fatigue crack growth in $2\frac{1}{4}$Cr-1Mo steel at 50 Hz in moist air and dry hydrogen gas (R = 0.30). Onset of marked hydrogen-assisted growth occurs at K^T_{max} = 22 MPa$\sqrt{m}$, ΔK^T = 15 MPa$\sqrt{m}$.

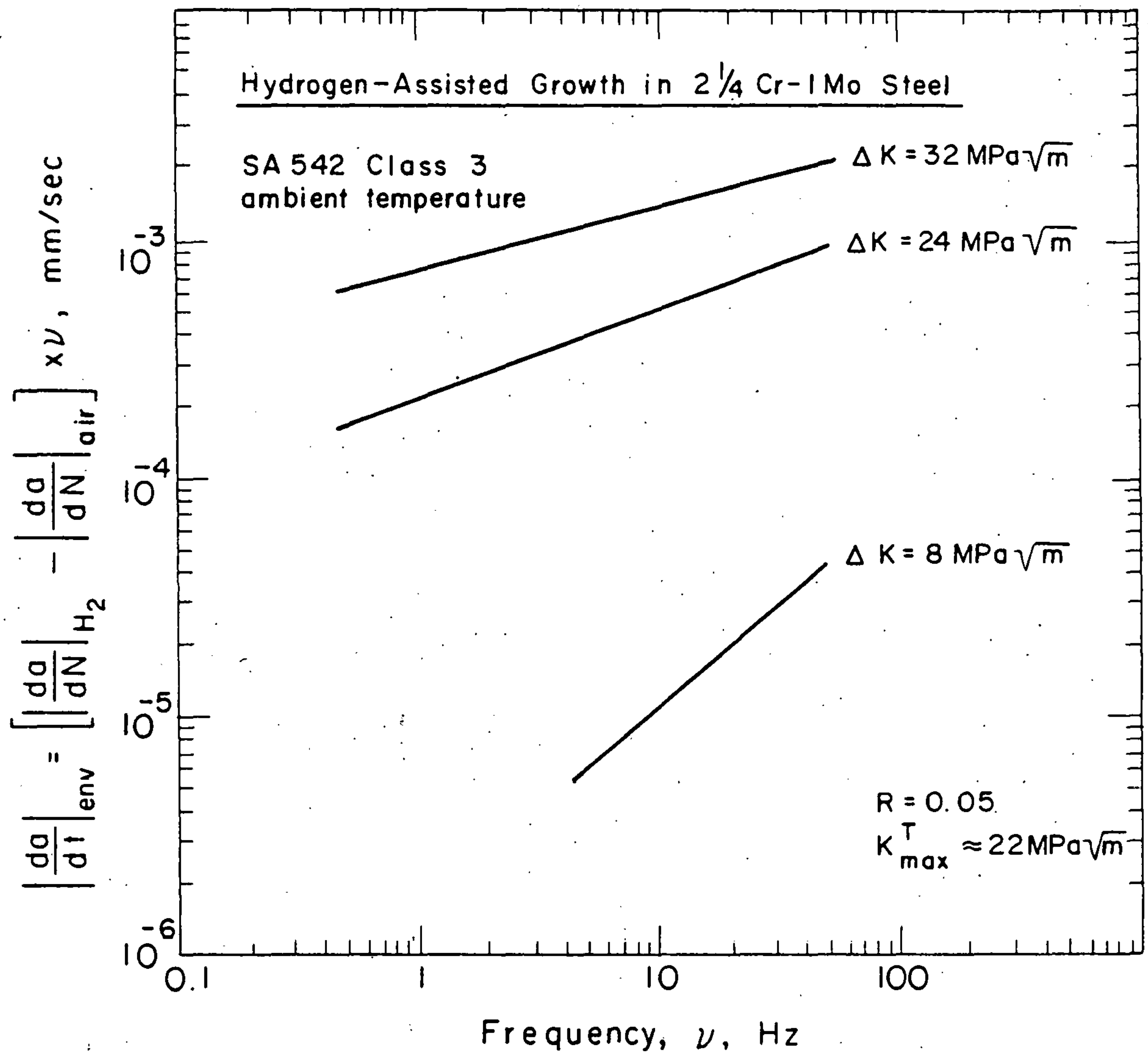

Fig. 14: Effect of frequency (ν) on environmental crack growth component $(da/dt)_{env}$ in SA542-3.

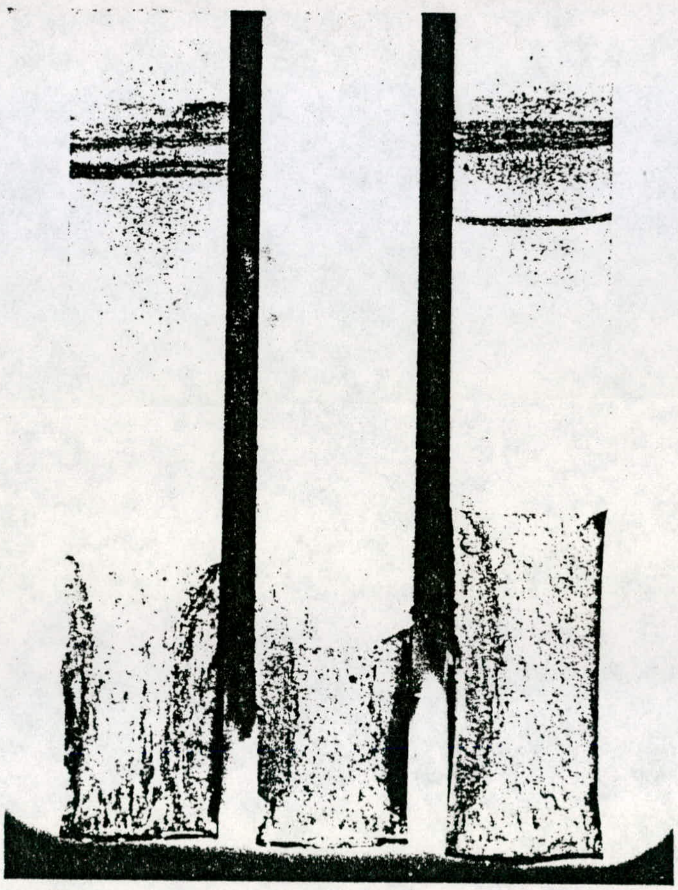

Fig. 15: Example of bands of corrosion deposit observed where growth rates were near-threshold. Specimen b) represents crack growth exceeding 10^{-5}mm/cycle.

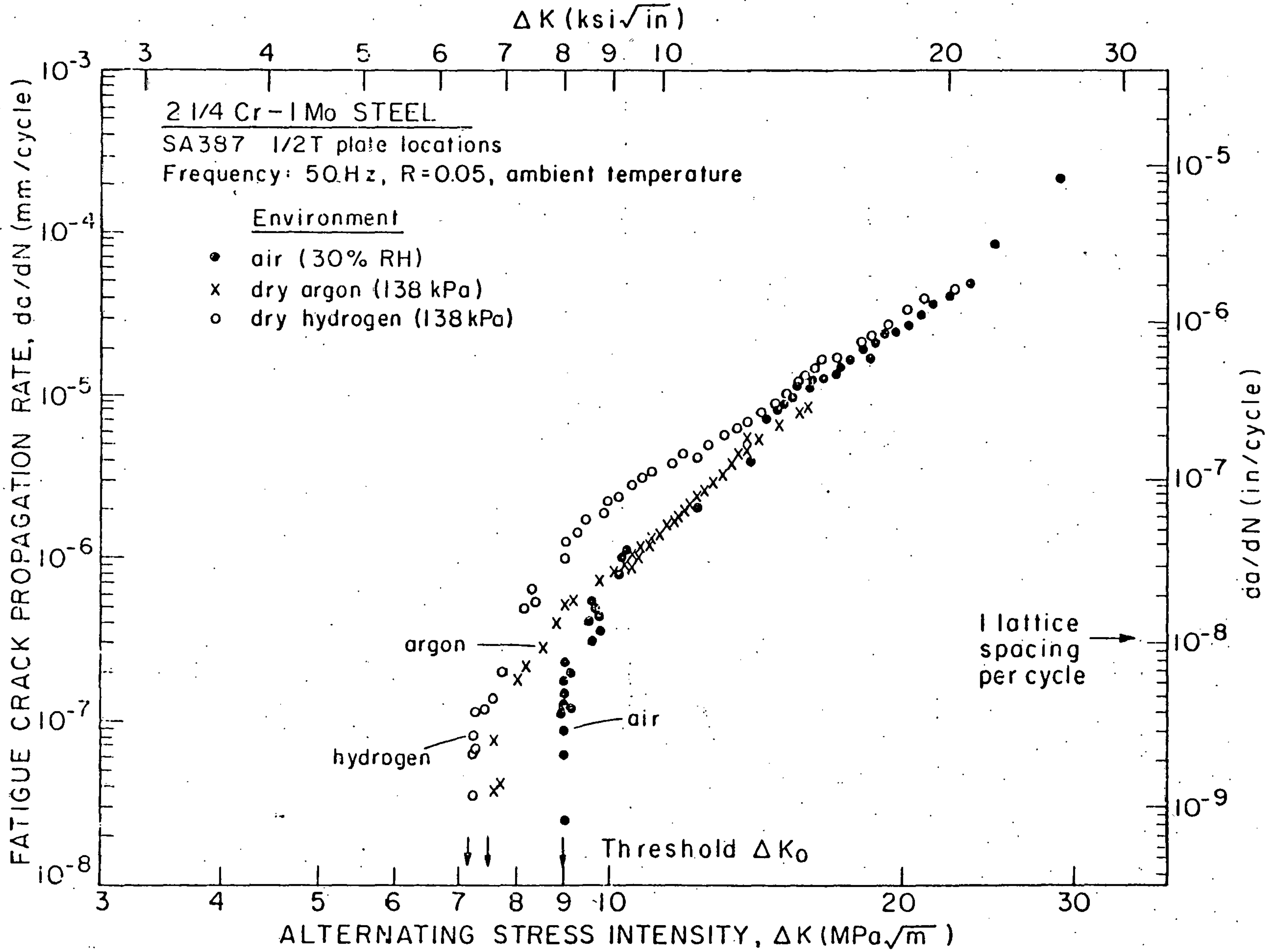

Fig. 16: Fatigue crack propagation data for normalized 2¼Cr-1Mo steel tested at R=0.05 (50 Hz) in moist air, dry hydrogen and dry argon.