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QUANTITATIVE OBSERVATIONS OF HYDROGEN-INDUCED, SLOW CRACK GROWTH IN A LOW ALLOY STEEL

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ABSTRACT

Environmental hydrogen embrittlement of iron base alloys is a complex phenomenon and is shown in this study to remain complex even under systematic investigation in simple, well-characterized environments using a single alloy system and a single test technique. Hydrogen-induced slow crack growth, da/dt, was studied in AISI-SAE 4130 low alloy steel in gaseous hydrogen and distilled water environments as a function of applied stress intensity, K, at various temperatures, hydrogen pressures, and alloy strength levels. At low values of K, da/dt was found to exhibit a strong exponential K dependence (Stage I growth) in both hydrogen and water. In hydrogen the value of K required to attain a given value of $(da/dt)_I$ was determined quantitatively and varied inversely with both hydrogen pressure and alloy strength level and directly with temperature. In water a similar strength level dependence was observed; however, K for a given $(da/dt)_I$ was found to be essentially independent of test temperature. At intermediate values of K, da/dt exhibited a small but finite K dependence (Stage II), with the Stage II slope being greater in hydrogen than in water. In hydrogen, at a constant K, $(da/dt)_{II}$ varied inversely with alloy strength level and varied essentially in the same complex manner with temperature and hydrogen pressure as noted previously. In water at a constant value of K, $(da/dt)_{II}$ was also inversely related to alloy strength level and was a complex function of temperature. The results of the present study provide support for most of the qualitative predictions of the lattice decohesion theory as recently modified by Oriani. The lack of quantitative agreement between data and theory and the inability of theory to explain the observed pressure dependence of slow crack growth are mentioned and possible rationalizations to account for these differences are presented.

INTRODUCTION

Hydrogen originating from its equilibrium position within the metal lattice, from a gaseous hydrogen environment in contact with the metal, or from the product of a heterogeneous surface reaction can strongly influence the fracture behavior of body-centered-cubic iron base alloys. This influence occurs primarily through a reduction in the ability of the metal to adsorb energy during either the initiation or growth stages of fracture.

Most hydrogen embrittlement processes are extremely complex, particularly when the embrittling species orginates in the environment. Hydrogen must not only interact with the metal lattice to reduce its energy adsorbing ability, but it must also be transported from its origin in the environment to the location where this interaction can occur. In fact, these latter processes, the kinetic or rate processes, can be as important as the interaction processes and under many conditions can control the rate or severity of embrittlement. From an engineering standpoint, it is many times the knowledge and/or control of these kinetic processes which will permit a potentially susceptible alloy to be used safely in a critical structure exposed to a hydrogen environment.

Any theory which adequately explains the overall processes of embrittlement must include both the kinetic as well as the mechanistic aspects. Spiedel(1) postulates the following five points to be necessary in the development of such a theory:

(1) Qualitative observation of the phenomenon.

(2) Systematic quantitative measurements of the phenomenon.

(3) A plausible working hypothesis.

(4) Development of the working hypothesis into a quantitative theory.

(5) Comparison of the theoretical predictions with the quantitative experimental observations.

As can be seen from the volume and content of the papers presented at this conference alone, we are well on the road to the development of a working theory. There are a great number of excellent qualitative observations and an adequate number of plausible working hypotheses, with some approaching a semi-quantitative state. What is needed, however, are reliable quantitative measurements that can be compared with these theories.

Numerous experimental investigations have been made to understand the phenomenon of hydrogen embrittlement. These are motivated both by the large number of service failures attributed to hydrogen embrittlement and by the increasing technological importance of hydrogen. Unfortunately, however, a vast majority of the investigators have studied the influence of hydrogen on such properties as tensile elongation, ultimate strength, and notch strength. These investigations have been useful for screening materials, processes or environments, but because of their qualitative nature, they have done little to increase our understanding of the specific embrittlement mechanism. The tensile properties of metals are qualitative because they involve such a variety of interrelated factors that the hydrogen-sensitive factors cannot be isolated.

The development of fracture mechanics has resulted in a better understanding of fracture processes. It has become apparent that some parameter(s) associated with the crack growth stage of fracture affords the most promising quantitative measure of embrittlement. In a hydrogen environment, crack growth occurs under the combined influence of hydrogen and stress at the crack tip. If the crack tip stress can be defined adequately, crack growth rate becomes a quantitative measure of environmental influence. Linear elastic fracture mechanics provides at least the basis for characterizing partially the crack tip stress by a single parameter known as stress intensity, K. Unfortunately, this analysis is not perfect for metals; metals are never truly elastic but invariably involve some plastic deformation at the crack tip. This characteristic presents some problems in the analysis of experimental data. Nevertheless, the relationship between the environment-induced crack growth rate, da/dt, and the applied stress intensity, K, serves as the best quantitative description of the embrittlement process.

It has recently been demonstrated that the general form of the curve for crack growth rate, da/dt, versus stress intensity, K, for iron base alloys in gaseous hydrogen(2-4) and in water(5) is similar to that observed for other metals(6) and environments,(1,7) as shown schematically in Fig. 1. The curve consists of three distinct stages: at low values of K, da/dt is strongly dependent on K (Stage I); at intermediate values of K, da/dt becomes relatively independent of K (Stage II); and as K approaches the critical value of stress intensity, K_c, da/dt increases rapidly (Stage III). Stages I and II are considered to arise from the chemical interaction between the environment and the metal lattice at or near the crack tip, with the mechanical influence on crack growth occurring primarily through the interaction with this chemical influence. From the form of Fig. 1 and multi-reaction rate theory,(8) assuming Stages I and II each represent a distinct rate process, the overall observed crack growth rate can be written as a simple function of the individual rates:

$$\frac{1}{\left(\frac{da}{dt}\right)_{\text{overall}}} = \frac{1}{\left(\frac{da}{dt}\right)_{I}} + \frac{1}{\left(\frac{da}{dt}\right)_{II}} \qquad (1)$$

where the individual processes are sequential in their operation, and with the slowest process controlling the overall rate. Stage III has been observed in in an inert environment.(9) Thus, it is not strongly dependent on interaction with the environment and is primarily a mechanical effect. For completeness, however, the overall crack growth rate over the full range of stress intensities of Fig. 1 can be expressed as a function of the three individual growth rates in the following manner:

$$\left(\frac{da}{dt}\right)_{\text{overall}} = \left[\frac{1}{\left(\frac{da}{dt}\right)_{I}} + \frac{1}{\left(\frac{da}{dt}\right)_{II}}\right]^{-1} + \left(\frac{da}{dt}\right)_{III} \qquad (2)$$

where Stages I and II are sequential processes and Stage III is parallel to the operation of the first two.

Most previous attempts at a quantitative experimental investigation of environmental hydrogen embrittlement have been incomplete and have not covered a sufficient range of stress intensities to include both Stage I and Stage II growth. For example, earlier studies(10,11) designed to reveal the processes involved in the low pressure gaseous hydrogen embrittlement of a high strength iron base alloy were restricted to a single applied stress intensity. These studies demonstrated the importance of kinetic processes to hydrogen-induced crack growth at that stress intensity, but were incapable of describing the overall process of crack growth under combined chemical and mechanical influences. It is a description of this relationship and the quantitative definition of the influence of parameters such as temperature, hydrogen fugacity, and yield strength on the relationship that are required for comparison in order to develop an overall theory of environmental embrittlement.

The purpose of this paper is to initiate a quantitative understanding of the chemical and mechanical influences involved in Stage I and Stage II crack growth in iron base alloys. We will review recent quantitative observations made on one iron base alloy as a function of temperature, pressure, and yield strength, when the alloy was exposed to environments of low pressure, high purity hydrogen and distilled water. An attempt will be made to develop quantitative relationships between da/dt and K, T, P_{H_2}, and σ_{ty} for Stage I and Stage II crack growth in hydrogen and water. We will compare these relations measured in the two environments in an attempt to separate the kinetic and mechanistic aspects of the embrittlement process. Next, we will discuss what is thought to be the most complete of the previously proposed theories on environmental hydrogen embrittlement. Finally, we will compare the predictions of this theory with the observed experimental data in an effort to elucidate the further theoretical development of an adequate, consistent theory of environmental embrittlement.

EXPERIMENTAL OBSERVATIONS

The experimental results summarized herein have recently been reported in detail as a NASA Technical Note.(12) Briefly, the material used in this study was commercially obtained AISI-SAE 4130 low alloy steel, having the nominal composition Fe-1 Cr-0.2 Mo-0.30 C. All specimens were water quenched from 843°C and tempered at temperatures between 250°C and 540°C for 2 hours to obtain the desired alloy strength. The crack growth rate studies were conducted on "double-torsion" (DT) type specimens as first described by Kies and Clark(13) and recently discussed in this application by Williams and Evans.(14) Tests were conducted at constant displacement, while the change in load was monitored with time. The instantaneous load and rate of change in load were used to compute the stress intensity and the crack growth rate, respectively. All data were analyzed using the least-squares method.

Those tests conducted in a hydrogen environment were performed in an all metal-sealed, stainless steel test chamber evacuated to less than 1×10^{-3} torr prior to backfilling with high purity hydrogen. The tests which were performed in distilled water (having a pH of approximately 6) were carried out under conditions of uncontrolled circuit potential.

Gaseous Hydrogen Environment

The general form of the variation of da/dt with K observed in the present study for 4130 steel in a high purity gaseous hydrogen environment is similar to that observed by others for other alloy systems.(2-4) Such a curve is shown in Fig. 2 and covers the full range of K values up to the critical stress intensity. For comparison, the data obtained by Hudak for 18 Ni (250) maraging steel are also shown on this curve.(3) Although these two iron base alloys have slightly different strength levels and were tested at somewhat different hydrogen pressures, the observed crack growth rates are comparable. Additionally, in Stage I, the K dependence of $(da/dt)_I$ appears similar; however, in Stage II, 4130 steel exhibits a finite K dependence, unlike maraging steel in which $(da/dt)_{II}$ appears independent of K. Such a variation in the K dependence of $(da/dt)_{II}$ with the alloy system is not unexpected for iron base alloys. Similar behavior has been repeatedly observed in water environments and has been discussed in detail by Carter.(5)

In 4130 steel, $(da/dt)_I$ exhibited a strong (but still finite) K dependence down to at least 1×10^{-8} m s^{-1}, which was the resolution of this study. Because of the very limited range of K involved in Stage I growth, the exact functional relation could not be definitely established. As seen in Fig. 2, however, the data do appear to obey an exponential relationship, at the least to a good approximation, and thus can be expressed by the proportionality:

$$(da/dt)_I \propto \exp K \tag{3}$$

In Stage II, $(da/dt)_{II}$ is seen from Fig. 2 to be much less dependent on K than $(da/dt)_I$ and is typical of most data of this study. It will be seen, however, that when the experimental conditions are such that Stage II growth occurs at values of K approaching the critical stress intensity, $(da/dt)_{II}$ becomes significantly more dependent on K. This relation is the exception and will be discussed in detail in a later section. Again, because of the limited range of data, some ambiguity exists as to the exact functional form which best describes Stage II. By the least-squares method, the K dependence of $(da/dt)_{II}$ was found to be equally well expressed by either an exponential or a power relationship:

$$(da/dt)_{II} \alpha \exp 0.1 K \tag{4}$$

or

$$(da/dt)_{II} \alpha K^{3.5} \tag{5}$$

As mentioned previously, this observed K dependence of Stage II growth differs from the K independence previously observed for 18 Ni (250) maraging steel(3) and indicated for H-11 steel.(2)

The fracture surfaces of failed specimens were analyzed using a scanning electron microscope (SEM). Figures 3 through 6 are scanning electron micrographs of typical fracture surfaces associated with crack growth at decreasing applied stress intensities for one of the 4130 steel specimens of Fig. 2. These figures are consistent with previous observations;(2) it can be seen that the fracture mode appears to change from a ductile mode at high stress intensities to nearly total intergranular failure at low stress intensities. The fracture surface at high stress intensities (~ 45 MN $m^{-3/2}$) near the transition from Stage II to Stage III growth (Fig. 2), as seen in Fig. 3, contains large areas exhibiting multiple dimples (the normal ductile mode of failure for high strength steels), with a few areas less dimpled and somewhat intergranular. At moderate stress intensities (~ 32 MN $m^{-3/2}$), still in Stage II, fracture is associated with a fairly even mixture of ductile tearing and intergranular attack (Fig. 4). At low stress intensities (~ 25 MN $m^{-3/2}$) in Stage II, fracture appears to be primarily by intergranular failure with some evidence of ductile failure (Fig. 5). Finally, in Stage I (Fig. 6), fracture is intergranular with some minor deformation evidence on the intergranular facets.

The Influence of Temperature

The K dependence of da/dt was studied at various temperatures in 77.3 kN m^{-2} hydrogen for 4130 steel which had been heat-treated to two strength levels. A summary of the data observed for the higher strength material (σ_{ty} = 1330 MN m^{-2}, σ_{tu} = 1600 MN m^{-2}) is shown in Fig. 7 and for the lower strength material (σ_{ty} = 1190 MN m^{-2}, σ_{tu} = 1310 MN m^{-2}) in Fig. 8. As can be seen in these figures, for a constant crack growth rate, Stage I occurs at increasing values of K with increasing temperature. This effect is better seen in Fig. 9, which is a plot of the log K observed for Stage I (at a constant crack growth rate of 1×10^{-8}m s^{-1}) versus log test temperature. These data yield the following proportional relationships: for high strength material (σ_{ty} = 1330 MN m^{-2})

$$(K)_I \; \alpha \; T^{2.0}$$

and for lower strength material (σ_{ty} = 1190 MN m^{-2})

$$(K)_I \; \alpha \; T^{1.4}$$

From these equations, $(da/dt)_I$ can be approximately described by the relation:

$$(da/dt)_I \propto \exp(K/T^n) \qquad (6)$$

where n equals 2 at the higher strength levels and decreases somewhat as yield strength decreases. This observed temperature dependence is significantly greater than that suggested by the limited data of the previous studies on 18 Ni (250) maraging steel(3) and H-11 steel.(2)

In order to establish whether or not the temperature dependence of Stage I is the result of some irreversible process such as surface contamination or plastic deformation at the crack tip, a specimen containing a propagating crack in Stage I was cooled as rapidly as possible from a high temperature to a low one. The data are summarized in Fig. 10. The solid curves in this figure were taken from Fig. 7. The crack was allowed to propagate at 102°C under decreasing K, well into Stage I. At a K of approximately 33 MN $m^{-3/2}$, the specimen temperature was changed to 24°C as rapidly as possible (< 5 min). Immediately, da/dt was observed to increase from 1×10^{-7} m s^{-1} with decreasing temperature, reaching a value of 7×10^{-5} m s^{-1} at 24°C with no resolvable hesitation or delay time.

Stage II crack growth over most of the temperature range of this study was similar in form for both materials. The higher strength material exhibited a much greater rate of crack growth at any given value of K than did the lower strength material. However, as Stage II moved to higher values of K at high temperatures, the K dependence of $(da/dt)_{II}$ exhibited anomalous behavior and increased rapidly. Excluding this anomalous behavior, it is seen in Figs. 7 and 8 that for a given value of K, $(da/dt)_{II}$ is a complex function of temperature. As the temperature increases, the rate of Stage II growth for both strength levels first increases, goes through a maximum, and then decreases. This effect is more clearly presented in the form of Arrhenius plots, which are shown in Fig. 11. The form and slopes of the two curves shown were determined to be the best fit curves when both sets of data were combined, and are identical. Assuming that the data at high temperatures (Region I) and low temperatures (Region III) obey Arrhenius relations, the heat of reaction at high temperatures is approximately -54,300 J mole^{-1} and at low temperatures is 16,700 J mole^{-1}. Additionally, it is seen from Fig. 11 that the temperature at which the maximum crack growth rate is observed (Region II) shifts to lower temperatures as the strength level of the material decreases. The observed temperature dependence of $(da/dt)_{II}$ at low temperatures agrees well with that previously determined for 4130 steel(10) and that observed for 18 Ni (250) maraging steel.(3) The temperature dependence at high temperatures is, however, greater than that originally observed for 4130 steel(10) and less than that indicated for 18 Ni (250) steel.(3) The overall functional dependence of $(da/dt)_{II}$ on K can be expressed in a form similar to that previously suggested(10) and is given by

$$\left(\frac{da}{dt}\right)_{II} \alpha \left(\frac{\exp(72000/RT)}{m + \exp(72000/RT)}\right) \exp(-16700/RT) \qquad (7)$$

where m is some constant.

The Influence of Hydrogen Pressure

The K dependence of da/dt was studied as a function of hydrogen pressure at three temperatures corresponding to the three regions of Stage II crack growth (Fig. 11). The material examined had a yield stress of 1330 MN m^{-2} and an ultimate stress of 1600 MN m^{-2}. These data are summarized in Figs. 12, 13 and 14 for temperatures of -43, 25, and 75°C, respectively. It is seen from these figures that variations in hydrogen pressure were found to influence the stress intensity at which Stage I was observed; the magnitude of $(da/dt)_{II}$ at a constant K in Stage II was also affected.

The hydrogen pressure dependence observed for Stage I growth is better seen in Fig. 15, which is a plot of the logarithm of K observed for Stage I (at a constant crack growth rate of 1×10^{-6} m s^{-1}) versus log hydrogen pressure for crack growth at each of the three test temperatures. The analysis of each data set at each temperature resulted in the same functional relationship, which is given by the proportionality:

$$(K)_I \; \alpha \; P_{H_2}^{-0.2}$$

or from equation (3), in terms of crack growth rate,

$$\left(\frac{da}{dt}\right)_I \; \alpha \; \exp\left(P_{H_2}^{0.2}\right) \tag{8}$$

These observations on Stage I growth are qualitatively similar to the trend of the pressure dependence indicated in the study on 18 Ni (250) maraging steel.(3)

The influence of hydrogen pressure on Stage II crack growth (Figs. 12, 13 and 14) is better seen in Fig. 16. This figure is a plot of log $(da/dt)_{II}$ at a constant K (40 MN $m^{-3/2}$) versus log hydrogen pressure at each of the three test temperatures. Analysis of each set of data yield:

at -43°C (Region III)

$$(da/dt)_{II} \; \alpha \; P_{H_2}^{0.56} \tag{9}$$

at 24°C (Region II)

$$(da/dt)_{II} \alpha P_{H_2}^{1.2} \tag{10}$$

and at 75°C (Region I)

$$(da/dt)_{II} \alpha P_{H_2}^{1.48} \tag{11}$$

If the above expressions are approximated by $P^{0.5}$, P^{1} and $P^{1.5}$, respectively (as previously suggested(10)), they can be substituted into equation (7) to obtain the general expression

$$\left(\frac{da}{dt}\right)_{II} \alpha \left(\frac{P_{H_2} \exp(72000/RT)}{m' + P_{H_2} \exp(72000\ RT)}\right) P_{H_2}^{0.5} \exp(-16700/RT) \tag{12}$$

This relation is similar to that previously determined for 4130 steel(10) and in part verified for 18 Ni (250) maraging steel(3) in Region III and for H-11 steel(2) in Regions I and II.

Finally, in an effort to establish if Stage I growth is the sole result of an applied fugacity (hydrogen pressure), as suggested by Oriani and Josephic,(15) or is the result of other influences, a crack propagating at one pressure in Stage I was rapidly exposed to a higher hydrogen pressure. These data are summarized in Fig. 17. The solid curves were taken from Fig. 13. The crack was allowed to propagate under decreasing K from Stage II well into Stage I at a hydrogen pressure of 11.2 kN m^{-2}. At a constant stress intensity of about 23 MN $m^{-3/2}$, the hydrogen pressure was rapidly (≈ 5 sec) raised to 77.3 kN m^{-2}. The crack growth rate immediately increased from 7.8×10^{-8} to 2.25×10^{-5} m s^{-1} with no observable hesitation or delay time.

The Influence of Alloy Strength Level

The K dependence of da/dt was studied in hydrogen at room temperature as a function of alloy strength level. These data are summarized in Fig. 18. It is seen that both Stage I and Stage II growth are influenced by variations in strength level. In Stage I, the stress intensity needed to obtain a given da/dt was found to increase as alloy strength was decreased. This relationship is better seen in Fig. 19, which is a plot of log K (observed at a constant da/dt of 1×10^{-8} m s^{-1}) versus the log of the tensile yield strength and ultimate strength. These data yield the following relations:

$$(K)_I \;\alpha\; \sigma_{ty}^{-5.2}$$

and

$$(K)_I \;\alpha\; \sigma_{tu}^{-3.6}$$

or from equation (3), in terms of approximate yield strength:

$$(da/dt)_I \;\alpha\; \exp \sigma_{ty}^{5} K \qquad (13)$$

In Stage II, the crack growth rate at a given value of K is seen to be a strong function of strength level, with $(da/dt)_{II}$ decreasing with decreasing strength level. At the higher strength levels the K dependence of (da/dt) appears nearly constant; however, at the lower strength levels, it increases significantly. This relationship is similar to the anomalous behavior previously discussed for Stage II growth at high temperatures (Figs. 7 and 8). These data for Stage I and Stage II crack growth are similar to the trends observed by Hudak in a comparison of hydrogen-induced crack growth in 18 Ni (250) and 18 Ni (300) maraging steels.(3)

Water Environment

The K dependence of da/dt in distilled water was studied in 4130 steel as a function of temperature and at two strength levels. Although similar studies have been performed on other iron base alloys,(5) the present study was conducted using identical material, heat treatments, and test techniques, so that the influences of a water environment and a gaseous hydrogen environment could be quantitatively compared.

The Influence of Temperature

The observed K dependence of da/dt in water at various temperatures is summarized in Fig. 20 for 4130 steel having a yield stress of 1330 MN m^{-2} and an ultimate stress of 1600 MN m^{-2}. As is seen from this figure, the forms of these curves are similar to those observed for this material in a hydrogen environment (Fig. 7). Stage I growth at each test temperature exhibits a strong (but still finite) dependence on K. The value of K required to obtain a given da/dt appears nearly independent of test temperature. At a da/dt of 1×10^{-7} m s^{-1}, the value of K is found to be approximately 16 MN $m^{-3/2}$. This value is slightly less than that observed in hydrogen near one atmosphere at room temperature and is similar to the "threshold" value observed in water for a number of other alloy systems.(5)

Stage II crack growth in water is seen in Fig. 20 to be K dependent. Analysis of each data set at temperatures between 12 and 53°C results in nearly identical relationships. The functional relation between $(da/dt)_I$ and K may be expressed equally well by either of the following two proportionalities:

$$(da/dt)_{II} \propto e^{0.05K} \qquad (14)$$

or

$$(da/dt)_{II} \alpha K^{1.6} \tag{15}$$

Depending on the particular material and investigation, previous results indicate that the K dependence of Stage II growth varies from being independent of K to being linearly dependent.(5) Because of the limited range of data and inherent scatter in this type of test, the results of the present study could be interpreted as approaching a linear dependence.

In Stage II, da/dt at a constant value of K is seen from Fig. 20 to be a strong function of temperature. For comparison, $(da/dt)_{II}$ at 24°C observed in water (Fig. 20) is much slower than that for material having the same strength level but tested in hydrogen at a pressure of 77.3 kN m^{-2} (Fig. 7). At 72°C, however, $(da/dt)_{II}$ in water is seen to be faster than in hydrogen. As discussed previously, the maximum crack growth rate in hydrogen was observed to be approximately 1×10^{-4} m s^{-1} and occurred at some temperature near 24°C (Fig. 11). It appears from Fig. 20 that in water, the maximum $(da/dt)_{II}$ is approached at 72°C to 89°C and that this rate is also approximately 1×10^{-4} m s^{-1}. Figure 21 is an Arrhenius plot of these data at a constant K. From this figure it is seen that the best fit curve through these data is not a straight line; thus these data do not obey a single Arrhenius relation. This observation is inconsistent with the interpretation by other investigators of data on other alloy systems over a similar temperature range. Johnson and Willner(16) found the temperature dependence of Stage II growth in H-11 steel to obey an Arrhenius relation yielding an activation energy of 37,600 J $mole^{-1}$. Likewise, Van Der Sluys(17) deduced a similar relationship for an iron alloy very similar to AISI 4130, i.e., AISI 4340 steel. However, their data at lower temperatures tend to deviate from the suggested Arrhenius relation. It is possible that at least for 4130 steel, Stage II growth in water is a complex function of temperature, similar to that observed in hydrogen (Fig. 11). A least-squares analysis of the four data points at the lower temperatures suggests an energy of activation of 79,500 J $mole^{-1}$.

The Influence of Alloy Strength Level

The general influence of alloy strength level on Stages I and II crack growth in water was determined by comparing the K dependence of da/dt observed at 24°C in 4130 steel having a yield strength of 1330 MN m^{-2} and an ultimate strength of 1660 MN m^{-2} (Fig. 20) with that observed in material having yield and ultimate stresses of 1230 MN m^{-2} and 1390 MN m^{-2}, respectively. These data are summarized in Fig. 22. It is seen from this figure that both Stage I and Stage II growth in water are strongly influenced by alloy strength level. As the alloy strength decreases, K for a given $(da/dt)_I$ increases, and $(da/dt)_{II}$ for a given K decreases. The trend and magnitude of these effects are similar to those observed in a gaseous hydrogen environment (Fig. 18).

DISCUSSION

As may be seen from the results presented, embrittlement of iron base alloys by hydrogen and hydrogen producing environments is exceedingly complex, even when examined in a systematic manner in simple, well characterized environments using a single alloy system and a single test technique. Nevertheless, the main objective of this study has been accomplished: namely, to develop a set of quantitative data which can be compared with theory. It is well beyond the scope of this paper to attempt to analyze or discuss all of these results in terms of the many theories proposed by various authors. Instead, for illustrative purposes only, we will discuss the results in terms of one semi-quantitative theory. We will first present a brief description of this theory and next compare the predictions of the theory with the experimental data observed in the present study; we will indicate where theory and observation disagree and when possible, attempt to suggest modifications to the theory.

Theory

Historically, there have been three major mechanisms advanced to explain the detrimental influence of hydrogen on the iron lattice: (1) the planar pressure mechanism, (2) the surface energy mechanism, and (3) the lattice cohesion mechanism. The planar pressure model is generally accepted as an explanation for a specific form of hydrogen embrittlement, but it is not applicable to environmental embrittlement, at least not that caused by a low pressure gaseous hydrogen environment. The two remaining models are similar in that they both postulate a reduction in lattice strength by the presence of hydrogen--the difference being only in the predicted location of this interaction. Because of the lack of any real indication as to the quantity of hydrogen required to reduce the strength of a lattice, both of these models can be applied to environmental embrittlement, even low pressure gaseous hydrogen embrittlement.

Any complete theory of environmental embrittlement, however, must consider <u>both</u> the mechanism by which the energy adsorbing ability of a metal lattice is reduced by the presence of a chemical species and the kinetic processes involved in getting the chemical species from the environment to the point where it can interact with the metal lattice. The processes of interaction and species transport are distinguishable from one another in that the former is solely a function of the metal and the latter is a function of both the metal and the environment.

The overall kinetic process involved in the transport of hydrogen to the point where it can interact with the metal can be very complex, reflecting the original location and form of the hydrogen atom, the pressure and temperature of the test, as well as secondary considerations, such as impurities present in the environment. The importance of transport reactions to environmental embrittlement cannot be over-emphasized. If any one of the reaction steps involved in hydrogen transport is hindered or eliminated, the metal will be less susceptible to embrittlement and, in fact, may not exhibit embrittlement at all.

Oriani(18) has recently combined the mechanistic and kinetic aspects of environmental hydrogen embrittlement into what could be considered a semi-quantitative theory of hydrogen-induced cracking. It recognizes the essential argument of both the surface adsorption and the lattice decohesion models as a necessary, but not a sufficient condition for embrittlement. The essence of this approach is that a crack will grow in a metal when the local tensile stress, σ'_z, across the plane of the crack equals the maximum cohesive force, nF_m, of the metal lattice and that this force can be lowered by the stress-induced accumulation of hydrogen at this location. This process is described by the following two equations:

$$c'(\sigma'_z,\ f_H,\ da/dt)_M \geqq c'' \tag{16}$$

and

$$\sigma'_z = 2_\sigma (L/\rho)^{1/2} \geqq n\ F_m(c'') \tag{17}$$

Equation (16) states an important assumption of Oriani's theory: namely, that hydrogen-induced cracking will proceed only when the concentration of hydrogen at some point near the crack tip, c', reaches some critical concentration, c". As indicated in equation (16), the hydrogen concentration, c', will be a dynamic function of the following factors: the local tensile stress across the plane of the crack, σ_z'; the hydrogen fugacity, f_H; and the crack velocity, da/dt, as determined by the rate controlling mechanism, M. Equation (17) is a local failure criterion which, when satisfied, leads to local lattice decohesion. This criterion states that decohesion will occur when the local tensile stress, σ_z', (which at the tip of an elastic crack is equal to the indicated function of applied stress, σ, crack length, L, and crack-tip radius, ρ) is greater than, or equal to, the product of the reduced cohesive force of the metal-metal bond, $F_m(c")$ and the number of such bonds at the crack tip. This failure criterion is similar to both the Griffith equation for failure of elastic materials(19) and, more significantly, to the criterion proposed by Stoloff and Johnson(20) for environment-induced propagation of cracks. One important difference between Oriani's criterion and that of Stoloff and Johnson is that Oriani recognizes the dynamic character of the parameters ρ and $F_m(c")$ while Stoloff and Johnson consider only the static condition.

In order to discuss Oriani's model in terms of the data of this investigation, it is useful to rewrite equation (17) in terms of fracture mechanics parameters. As originally shown by Irwin(21), the stress intensity, K, is proportional to the limiting value of the elastic stress concentration factor, $2(L/\rho)^{1/2}$, as the root radius approaches zero. This would imply that for very sharp cracks (where ρ is small with respect to the crack depth)

$$K \propto 2\sigma(L/\rho)^{1/2} \geqq nF_m(c'') \qquad (18)$$

However, experimental data indicate that even for sharp cracks, fracture toughness values can be somewhat dependent on crack tip radius.(22) This effect is probably caused by the influence of tip radius on the plastic zone size. Therefore, it is reasonable to rewrite equation (18) as

$$K \geqq f(\rho)\ nF_m(c'') \qquad (19)$$

where $f(\rho)$, the proportionality constant, is an undefined function of ρ. It can be seen that this equation has the same general form as Oriani's failure criterion (equation 17). In equation (19), however, the failure criterion is stated in terms of K rather than σ_z' and it does not specify the functional dependence of K on ρ. For the remainder of this discussion, it will be assumed that equation (19) is equivalent to Oriani's failure criterion (equation 17).

From equation (19) and the assumptions given by equation (16), it can be seen that for a constant ρ, a threshold stress intensity will exist, below which no crack growth will occur; this threshold will be established by the value $n\ F_m(c'')$ and influenced by parameters influencing the concentration of hydrogen, c', in the metal lattice. The two distinct stages of crack growth (Stages I and II) are interpreted in terms of mixed control by kinetic processes. Stage I is assumed to involve the elastic interaction between hydrogen and the tensile stress field at the crack tip. Increasing the applied K results in an increase in the stress at the crack tip, as well as an increase in the hydrostatic stress in the lattice near the crack tip, an increase in the potential gradient for lattice diffusion, and thus, a lowering of $n\ F_m(c')$.

Stage I growth will have a finite K dependence, reflecting both the contributions of the raising of σ_z' and the lowering of $F_m(c')$. Stage II growth occurs when the crack growth rate becomes sufficiently rapid that an equilibrium subsurface hydrogen concentration can no longer be maintained, and the overall rate of hydrogen transport becomes determined by the input reactions in the gas phase or on the crack tip surface. If these controlling transport reactions are unaffected by the value of applied K, Stage II growth will reflect only the K dependence caused by increasing σ_z.

Comparison of Theory with Observation

A quantitative comparison of the theory of Oriani requires that we know the exact functional form of the parameters $f(\rho)$ and $F_m(c'')$. Unfortunately, forms of these parameters are not available to us at present and, thus, only a qualitative comparison between data of this study and the predictions of theory is possible.

As previously discussed, the theory of Oriani suggests that crack growth is the final result of a combination of chemical and mechanical factors. The instantaneous stress intensity is postulated to be a dynamic function of these factors as well as of the crack growth rate. Because Stage I and Stage II crack growth are distinctly separate from one another in both theory and experiment, we will discuss these stages separately. Stage I growth will be considered first and in greatest detail, for it is this behavior which has been least studied and which is least understood. Stage II growth will be more briefly discussed in the last section.

Stage I Growth

Oriani's model suggests that during Stage I crack growth, hydrogen in the metal lattice just below the crack tip surface is in equilibrium with hydrogen in the environment. Through the elastic interaction between this interstitial solute and the tensile stress at or ahead of the crack tip, hydrogen is transported to some location where the lattice cohesive force, $n\ F_m$, is lowered to $n\ F_m(c')$. For any fixed crack growth rate, the magnitude of this reduction is dependent on hydrogen fugacity. Therefore, for a fixed hydrogen fugacity (with all other experimental conditions remaining constant), crack growth will occur at stress intensities above some finite threshold value, K_{Th}. Such a K_{Th} was not observed in this investigation. For the 4130 steel, the Stage I curve appeared to have a finite (and apparently constant) slope for all stress intensities down to the lowest at which crack growth rates could be reliably measured ($\approx 10^{-8}$ m s^{-1}). However, this observation does not imply that a threshold may not exist at some still lower stress intensity; a threshold might be observed if crack growth rates could be reliably measured with greater sensitivity.

From Oriani's model, at a constant crack growth rate, increasing the hydrogen pressure should increase the hydrogen concentration in the lattice, decrease $F_m(c')$, and decrease K. This prediction is supported by the data at the three test temperatures of this study (Figs. (12), (13) and (14)). The rather strong pressure dependence of K in Stage I noted in this investigation is in agreement with the strong dependence measured by Oriani and Josephic.(15) It is not, however, what might be expected from a simple relationship between lattice concentration and environmental hydrogen pressure. From Sievert's law, it is logical to expect that the lattice concentration, and therefore the crack growth rate, should be proportional to $P_{H_2}^{0.5}$; however, the data of this investigation show

$K \alpha P_{H_2}^{-0.2}$, which through equation (3) is equivalent to a relationship between crack growth rate and hydrogen pressure of $(da/dt)_I \alpha \exp(P_{H_2}^{0.2})$, equation (8). This disagreement appears to constitute a major discrepancy between the model and experiment.

The large influence of hydrogen pressure (fugacity) on Stage I crack growth is dramatically demonstrated by an experiment originally proposed by Oriani(18) and later attempted by Oriani and Josephic.(15) A crack was allowed to propagate in 11.2 kN m^{-2} hydrogen under conditions of decreasing K until the observed crack growth rate was less than 1×10^{-7} m s^{-1} (which occurred at a value of K of 23 MN $m^{-3/2}$)(Fig. 17). The pressure of the environment was then rapidly increased to 77.3 kN m^{-2}, whereupon the crack growth rate immediately increased to 2.4×10^{-5} m s^{-1} (without the application of additional mechanical force or an associated period of incubation or acceleration). Cracking continued with a resulting decrease in K to a growth rate of 1×10^{-6} m s^{-1} and a K of 18.5 MN m^{-2}. These observations verify those made previously(15) and, as discussed by Oriani,(18) reinforce the idea that in Stage I at a constant K, not only a mechanical but a chemical (unstable) equilibrium exists between the specimen and its mechanical and chemical environment. They also appear to eliminate the possibility that Stage I is the result of such variables as surface contamination or is a result of variations in the crack tip radius, ρ (equation 19b).

The influence of temperature on Stage I crack growth can be seen in Figs. (7), (8) and (9). In hydrogen at a constant crack growth rate, K was found to increase significantly with increasing temperatures (Fig. (9) at a $(da/dt)_I$ of 10^{-8} m s^{-1}). Analysis of these data yield, for the higher strength material, $K \alpha T^{2.0}$, or through equation (3), $(da/dt) \alpha \exp(T^{-2.0})$; for the lower strength material, $K \alpha T^{1.4}$, or $(da/dt)_I \alpha \exp(T^{-1.4})$. Such functional relationships can only be explained by theory if $f(\rho)$ and/or $F_m(c')$ (equation (19b)) increase with temperature. In Fig. (20) it is seen that when material having the same strength is tested in water, K is relatively independent of temperature. Since the variable $f(\rho)$ can be assumed to be a mechanical rather than a chemical parameter, it should depend primarily on the metallurgical aspects of the material; therefore, it would appear that the observed difference between the behavior in hydrogen and that in water would eliminate $f(\rho)$ from being the variable predominantly responsible for the observed temperature dependence. An additional experiment was also performed which would appear to reinforce this view. A crack was allowed to propagate at a constant temperature of 102°C under conditions of decreasing K until the observed crack growth rate was less than 1×10^{-7} m s^{-1} and K had dropped to 33 MN m^{-2} (Fig. (10)). At this point, the temperature was decreased to 24°C as rapidly as possible ($<$ 5 min) whereupon the crack growth rate increased to 7×10^{-5} m s^{-1} without a detectable period of either incubation or acceleration. Since it is difficult to conceive of mechanisms by which decreasing the temperature would cause a blunted crack to become rapidly sharp, it appears that the parameter $f(\rho)$ cannot be the predominant term responsible for the observed temperature dependence of K. However, without knowing the form of the functional dependence of $F_m(c')$ on T, it is equally difficult to conceive that this parameter is responsible for the observed temperature dependence. In fact, it is logical, based on theory, to expect that the parameter is directly related to the rate of operation of some rate controlling mechanism. Since most such mechanisms are thermally activated, it is expected that increasing the temperature would increase the rate of reaction, increase the fugacity, and thereby decrease $F_m(c')$. This result would mean a decrease in K for a constant crack growth rate. This effect, of course, is the opposite to what is observed and again represents an apparent discrepancy between theory and experiment.

The observed influence of strength level on Stage I growth in hydrogen and water is seen in Figs. (18) and (22), respectively. The functional dependence is similar for the two environments and is described by the proportionality $K \alpha \sigma_{ty}^{-5}$. This behavior is in qualitative agreement with that predicted by the model. Decreasing the strength level of the alloy should increase the plasticity of the material, thus increasing $f(\rho)$. Additionally, decreasing the yield strength of the material could decrease the hydrogen fugacity by decreasing the elastic stress gradient and causing an increase in $F_m(c')$. Increases in both $f(\rho)$ and $F_m(c')$ would require an increased value of K to maintain a given crack growth rate.

As has been seen, there are areas of qualitative agreement and areas of apparent disagreement between Oriani's model and the data of this investigation. The data agree with the predictions of the model that $(da/dt)_I$ should be strongly dependent on K (because of the contribution of stress to both sides of equation (19)) and that the dependence should decrease at higher da/dt values, $(da/dt)_{II}$, when $F_m(c')$ becomes stress independent (because of rate limiting surface reactions). The model qualitatively predicts the observed increase in K (for a given $(da/dt)_I$) with decreasing yield strength. Points of apparent disagreement between the model and the data concern the effect of temperature and the effect of pressure on the stress intensity at a constant $(da/dt)_I$. These points will be briefly discussed below.

The data of this investigation as well as the work of previous investigators(2,3) suggest that the functional relationship between $(da/dt)_I$ and K has the form

$$(da/dt)_I = A' \exp(m'K) \tag{20}$$

Such a relationship has, in fact, been theoretically predicted by Liu(23) for an embrittlement model similar to Oriani's. His relationship for crack growth can be given as

$$(da/dt) = A \exp(mK/kT) \exp(\Delta H/kT) \tag{21}$$

where A is an undefined pre-exponential term, m is a parameter related to the interaction volume, ΔH is an apparent heat of reaction, k is the Boltzman constant, and T is absolute temperature. Rearranging equation (21) in the form of equation (19) gives

$$K = \frac{kT \ln[(da/dt)_I/A] - \Delta H}{m} \tag{22}$$

It can be seen that this equation is functionally equivalent to Oriani's failure criterion if

$$1/m = f(\rho)$$

and

$$kT \ln[(da/dt)_I/A] - \Delta H = F_m(c') \tag{23}$$

Assuming such a comparison is possible, equation (22) can be used to show qualitative agreement between Oriani's model and the observed temperature dependence of K. If the apparent heat of reaction, ΔH, is small with respect to $kT\ln[(da/dt)_I/A]$, then increasing the temperature should cause an increase in K (at a constant value of $(da/dt)_I$). This is the trend shown by the data for 4130 steel at both strength levels (Figs. (7) and (8)) in a gaseous hydrogen environment. However, equation (22) would never predict a temperature dependence greater than

$$K \propto T^1$$

unless m or A was also slightly temperature dependent. It is not unreasonable or in disagreement with the data of this investigation to expect that this might be the case. This, relationship then, could be more nearly consistent with the observed temperature dependence of K for cracking in hydrogen which was demonstrated in Fig. (9).

If, however, the apparent heat of reaction, ΔH, was large with respect to $kT\ \ln[(da/dt)_I/A]$, increasing the temperature would have only a negligible effect on $F_m(c')$ and the only effect of temperature on K would be due to any effect on $f(\rho)$ (i.e., $1/m$). This might be the case for the cracking of 4130 steel in water. This hypothesis is demonstrated graphically in Fig. (23) where the data of Fig. (9) as well as the data for K at $(da/dt)_I$ of 10^7 m s^{-1} from Fig. (20) are replotted on linear coordinates. The curves shown on Fig. (23) were constructed by estimating values of m from the data of Figs. (7), (8) and (23) at a temperature of 297°K and then making the following assumptions:

$$1/m = f(\rho) \propto T^{1/2}$$

$$A = f(T)$$

$$\Delta H \text{ for } H_2 = 25{,}000 \text{ J mole}^{-1}$$

and

$$\Delta H \text{ for } H_2O = 130{,}000 \text{ J mole}^{-1}$$

There is no specific basis for any of these assumptions except that they appear reasonable and produce a good fit between the curves and the data. The relatively good fit between the curves and the data means only that the model of Oriani (as well as the model of Liu(23)) is, at the least, qualitatively consistent with the relationship measured between K in Stage I and the test temperature for cracking in both hydrogen and water environments.

The observed effect of pressure on K in Stage I cannot be as easily reconciled with Oriani's model. As mentioned earlier, the observed increase in K with decreasing P_{H_2} is in qualitative agreement with the predictions of the model and in agreement with earlier observations.(15) However, the magnitude of the increase observed is difficult to reconcile with the assumption of equilibrium conditions. The equilibrium relationship between $(da/dt)_I$ and P_{H_2} predicted by Oriani's model would be

$$(da/dt)_I \; \alpha \; P_{H_2}^{1/2} \text{ at constant } K$$

which, by examining equation (3) or equation (21), can be seen to be equivalent to

$$K \; \alpha \; - 1/2 \ln P \tag{24}$$

at constant $(da/dt)_I$. This predicted behavior is significantly different from the measured relationship:

$$K \; \alpha \; P^{-0.2}$$

This difference remains as the only major discrepancy between the model of Oriani (applied to Stage I behavior) and the results of this investigation.

Stage II Growth

As has been discussed by several authors, the crack growth behavior observed at high stress intensities, defined as Stage II growth, is probably the result of some rate limiting transport reaction. Oriani has suggested in his model(18) that for high strength steels, this reaction is probably a surface reaction of a type similar to that originally proposed by Williams and Nelson.(10) The smaller K dependence of $(da/dt)_{II}$ is then the result of $F_m(c')$ being determined solely by this rate limiting surface reaction. If this surface reaction is independent of K, $F_m(c')$ would also be independent of K. Only the left hand side of the failure criterion (equation (19)) would be affected by K and the slope of the $(da/dt)_{II}$ versus K curve would be much smaller than the slope of Stage I. This situation is similar to what is observed in the present investigation in both hydrogen (Fig. 7) and water (Fig. 20).

The K dependence of $(da/dt)_{II}$ as a function of yield strength was observed to be nearly constant for σ_{ty} = 1330 MN m^{-2} to 1230 MN m^{-2}; however, at lower strength levels the slope was observed to increase with decreasing σ_{ty} (Fig. 18). This anomalous behavior is similar to the results of tests conducted at two strength levels in hydrogen as a function of temperature (Figs. 7 and 8) where the K dependence of $(da/dt)_{II}$ was relatively temperature independent for temperatures below some (apparently) critical value. Above these temperatures, however, the slope increased with increasing temperature. Finally, by comparing Figs. (7) and (20), it is seen that the K dependence of $(da/dt)_{II}$ is dependent on environment, with the slope in hydrogen (equation (6)) being about twice as large as the slope in water (equation (15)). The first two of these observations can be rationalized with the model of Oriani. Above some temperature and below some strength level, it is reasonable to expect an increased propensity for crack-tip blunting. This effect could cause a significant increase in $f(\rho)$ which would result in an increase in the Stage II slope. However, the effect of environment on the Stage II slope is not necessarily predicted by Oriani's model. This observation suggests that the slope is not entirely determined by the left hand component of equation (19b), but that it is dependent on some environment-sensitive parameter. If this suggestion is true, and if Stage II is actually a result of some surface reaction, this reaction must also be stress-dependent for at least one of the two environments.

The functional dependencies of $(da/dt)_{II}$ on T and P_{H_2} (equations (7) and (12)) are, in general, consistent with those initially reported for 4130 steel by the authors of the present paper.(10) Recently, similar observations have been reported by Sawicki,(2) Hudak,(3) and Kerns and Stachle(4) for other iron base alloys. Although the specific details of the kinetic processes responsible for the Stage II region are in dispute,(24,25) there is general agreement that this stage of growth is controlled by some process(es) occurring at the crack tip surface. The only difference between the results of this investigation and those of the earlier investigation (10) (both on 4130 steel) for Stage II growth is that the apparent heat of reaction at high temperatures (Region I) was greater in the present study than that measured earlier. Thus the apparent heat of reaction at high temperatures for 4130 steel more nearly equals that measured by Hudak for 18 Ni (250) maraging steel;(3) however, it is in poorer agreement with that measured by Sawicki for H-11 steel.(2)

One additional difference was noted in this study for the Stage II behavior of 4130 steel as compared to the previously observed behavior of 18 Ni (250) maraging steel(3) and H-11 steel.(2) In hydrogen, the Stage II growth for 4130 steel was found to exhibit a finite slope, whereas in the other two materials, Stage II appears truly independent of K. In water, 4130 steel also exhibits a finite slope, as does H-11 steel,(5) but 18 Ni (250) maraging steel does not.(5,26) This seemingly inconsistent behavior is not predicted by Oriani's model and may be the result of secondary influences such as crack branching, as suggested by Carter.(5)

In general, it can be stated that while Oriani's model does not actually address itself in detail to Stage II growth, the results of this investigation for Stage II are consistent with the theory. The only unexpected Stage II result was the observed effect of the Stage II slope on environment. However, while not actually predicted by the model, this behavior is not inconsistent if the controlling surface mechanism is postulated to be stress-sensitive.

CONCLUDING REMARKS

The prime objective of this study was accomplished: to develop a set of quantitative experimental results which might be used as a basis for developing and/or verifying a quantitative theory of hydrogen embrittlement. Slow crack growth rate (da/dt) versus stress intensity (K) curves were obtained for AISI-SAE 4130 low alloy steel exposed to either high purity, gaseous hydrogen or distilled water environments; the curves were obtained as a function of strength level, hydrogen pressure, and temperature. As a first attempt at comparing data with theory, the data of this study were compared with the qualitative predictions of the lattice decohesion theory as recently modified by Oriani. These data provide some support for the basic ideas of this theory; however, the pressure dependence of Stage I crack growth observed in this study cannot be explained in terms of Oriani's analysis of the embrittlement process.

REFERENCES

1. M. O. Speidel. "The Theory of Stress-Corrosion Cracking in Alloys". (J. C. Scully, ed.) Brussels (NATO Scientific Affairs Division) (1971) p. 289.
2. V. R. Sawicki. "Hydrogen Induced Cracking in a High Strength Steel". Ph.D. Dissertation, Material Science Center, Cornell University (1971).
3. S. J. Hudak, Jr. "The Kinetics of Hydrogen Enhanced Crack Growth in High Strength Steels". M. S. Thesis, Metallurgy and Material Science, Lehigh University (1972).
4. G. E. Kerns and R. W. Staehle. Scripta Met., 6, 631 (1972).
5. C. S. Carter. Engr. Fract. Mech., 3, 1 (1971).
6. D. P. Williams and H. G. Nelson. Met. Trans., 3, 2107 (1972).
7. J. A. Feeney and M. J. Blackburn. "The Theory of Stress-Corrosion Cracking in Alloys". (J. C. Scully, ed.) Brussels (NATO Scientific Affairs Division) (1971) p. 355.
8. H. G. Nelson. "The Kinetic and Mechanical Aspects of Hydrogen-Induced Failure in Metals". NASA TN D-6691, National Aeronautics and Space Administration (1972).
9. J. E. Collipriest. "Part-Through-Crack Fracture Mechanics Testing". Report SD 71-319, North American Rockwell (1971).
10. D. P. Williams and H. G. Nelson. Met. Trans., 1, 63 (1970).
11. H. G. Nelson, D. P. Williams, and A. S. Tetelman. Met. Trans., 2, 953 (1971).
12. H. G. Nelson. To be published as NASA TN, National Aeronautics and Space Administration (1973).
13. J. A. Kies and B. J. Clark. "Fracture - 1969". (P. L. Pratt, ed.), Chapman and Hall, London (1969) p. 483.

14. D. P. Williams and A. G. Evans. Accepted for publication in J. Testing & Materials, May (1973).

15. R. A. Oriani and P. H. Josephic. Scripta Met., 6, 681 (1972).

16. H. H. Johnson and A. M. Willner. Appl. Mater. Res., 4, 34 (1965).

17. W. A. Van Der Sluys. "Mechanisms of Environment Induced Subcritical Flow Growth in AISI 4340 Steel". T&AM Report No. 292, Department of Theoretical and Applied Mechanics, University of Illinois (1966).

18. R. A. Oriani. Berichte der Bunsen Gesellschaft für Physikalische Chemie, Proc. Conf. on Hydrogen Metals, Jülich (1972).

19. A. A. Griffith. Philosophical Transactions Royal Soc. (London), Series A, 221, 163 (1920).

20. N. S. Stoloff and T. L. Johnson. Acta Met., 11, 251 (1963).

21. G. R. Irwin, in "Proceedings First Symposium on Naval Structural Mechanics", Pergamon Press, London and New York, N. Y., (1960).

22. V. Weiss and S. Yukawa, "Fracture Toughness Testing and Its Applications". ASTM STP 381, New York, N. Y. (1965) p. 1.

23. H. W. Liu. Trans. ASME, J. Basic Engrg., D, 633 (1970).

24. R. A. Oriani. Met. Trans., 1, 2346 (1970).

25. V. Sawicki and H. H. Johnson. Met. Trans., 2, 3496 (1971).

26. S. Mostovoy, H. R. Smith, R. G. Lingwall, and E. J. Ripling. Engrg. Fract. Mech., 3, 291 (1971).

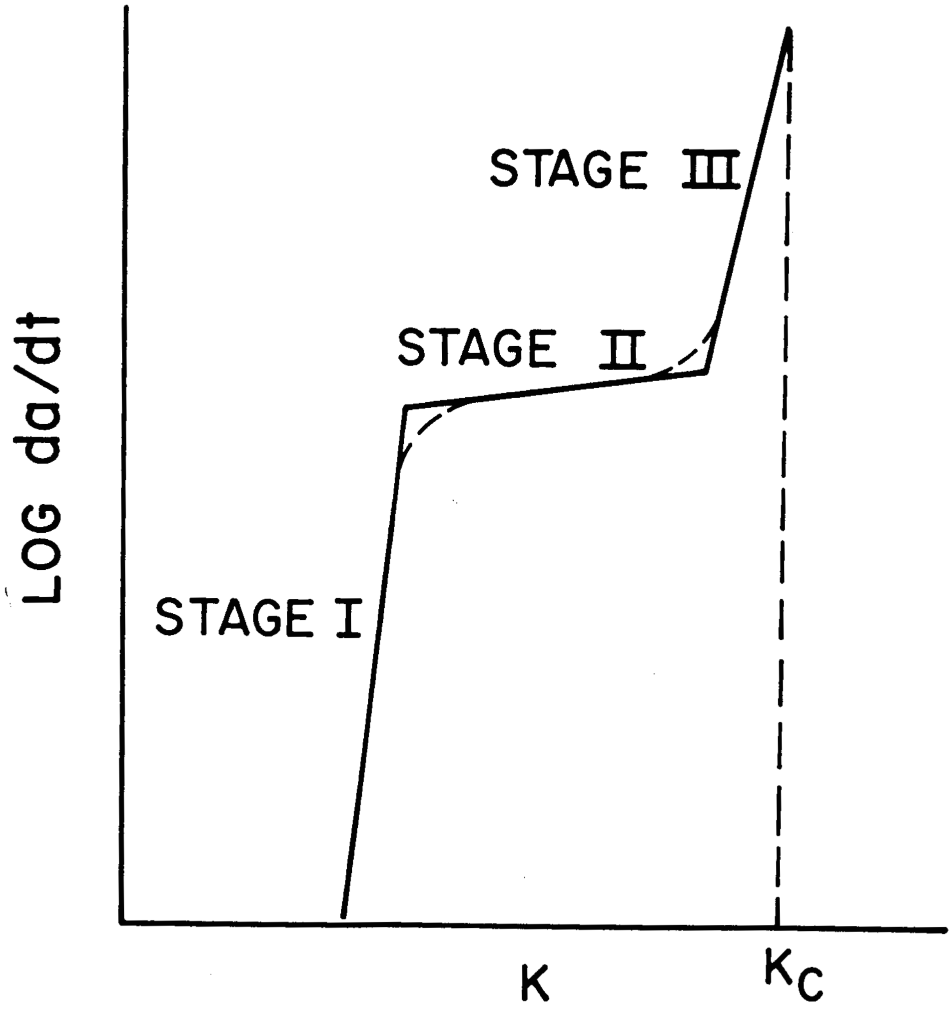

Fig. 1. - General form of environment-induced crack growth as a function of applied stress intensity.

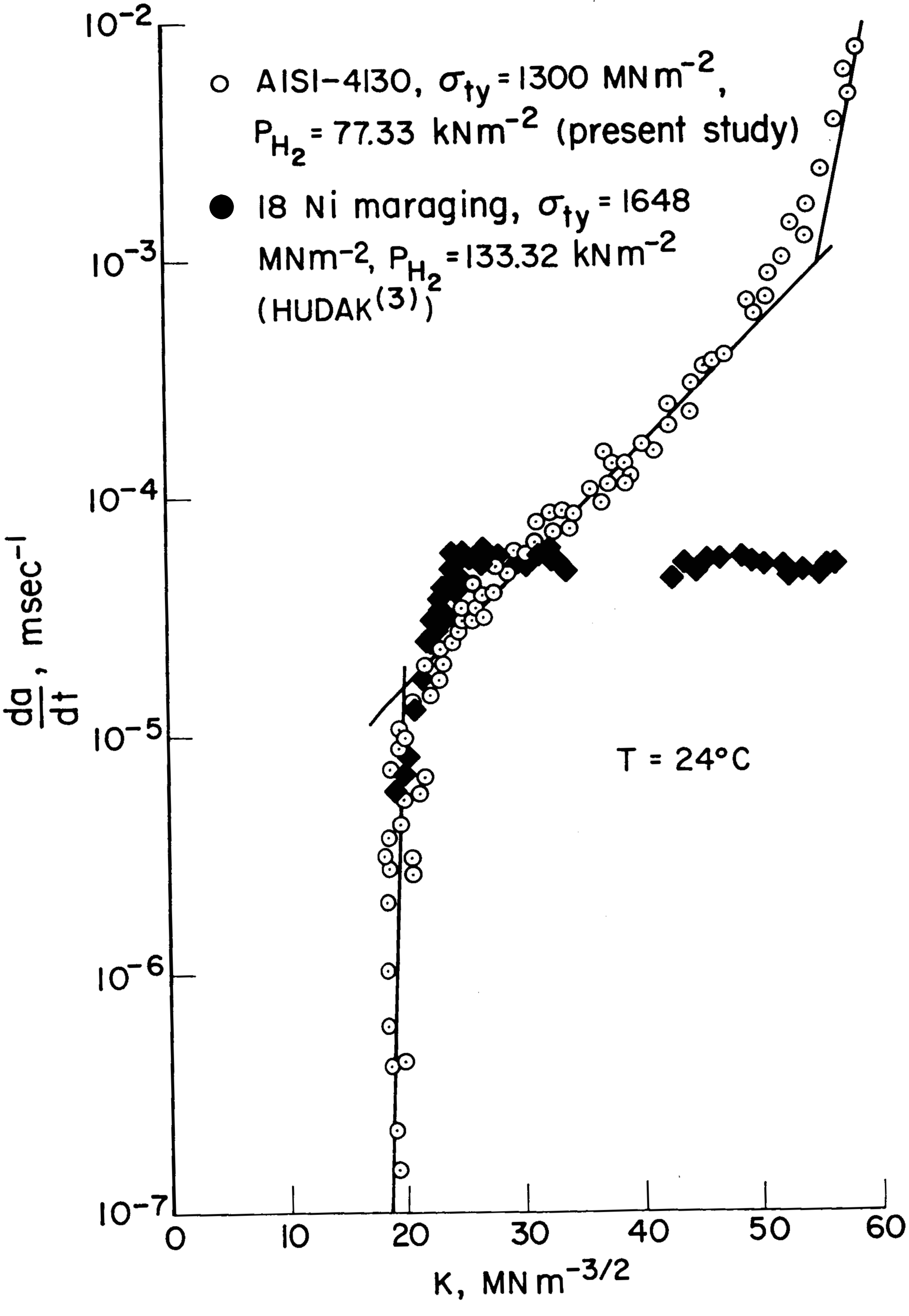

Fig. 2. - Hydrogen-induced crack growth as a function of applied stress intensity for hardened 4130 steel and 18 Ni (250) maraging steel.

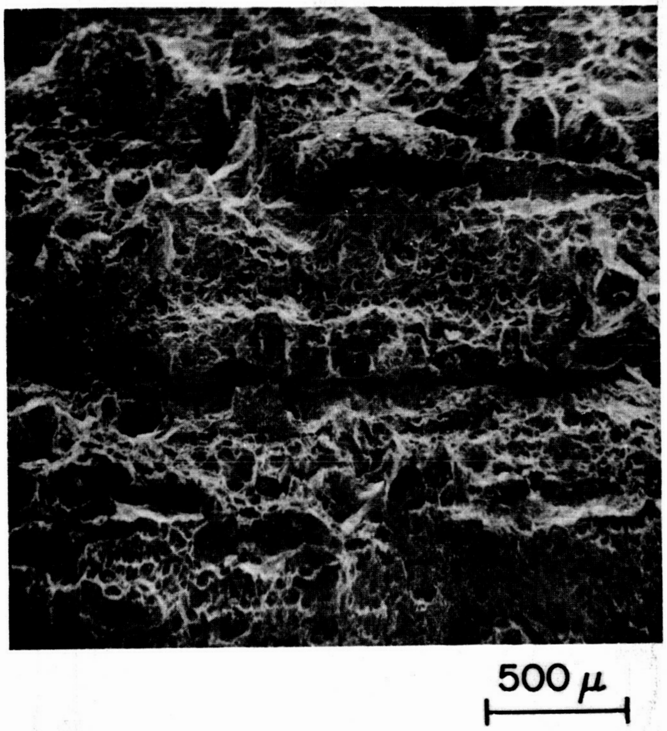

Fig. 3. - SEM micrograph of the fracture surface of the portion of a specimen failed in the transition region between Stage II and Stage III.

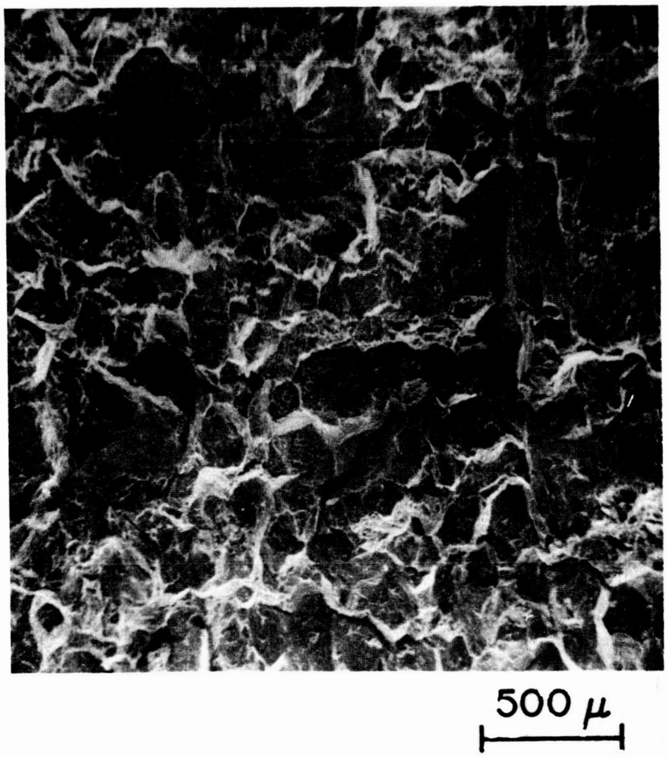

Fig. 4. - SEM micrograph of the fracture surface of the portion of a specimen failed mid-range of Stage II.

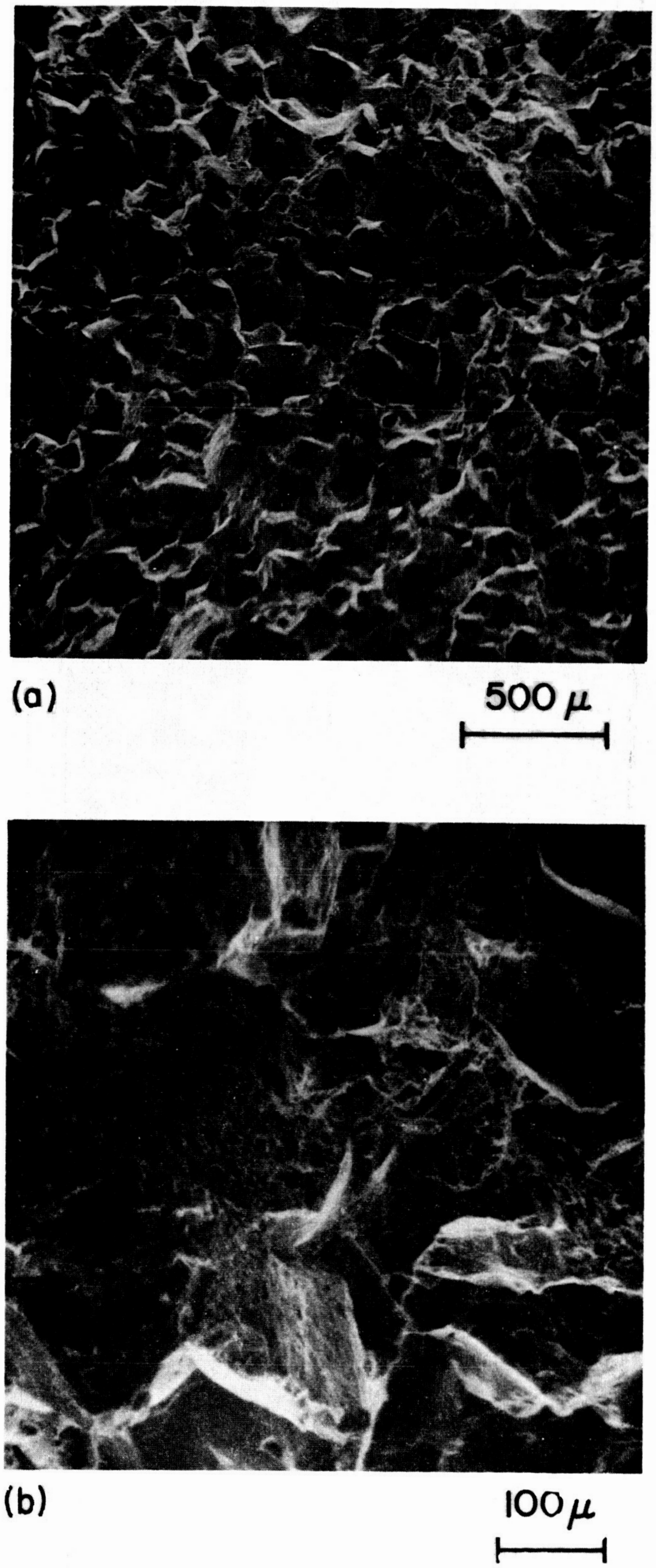

Fig. 5. - SEM micrograph of the fracture surface of the portion of a specimen failed in Stage II near Stage I transition; (a) low magnification, (b) high magnification.

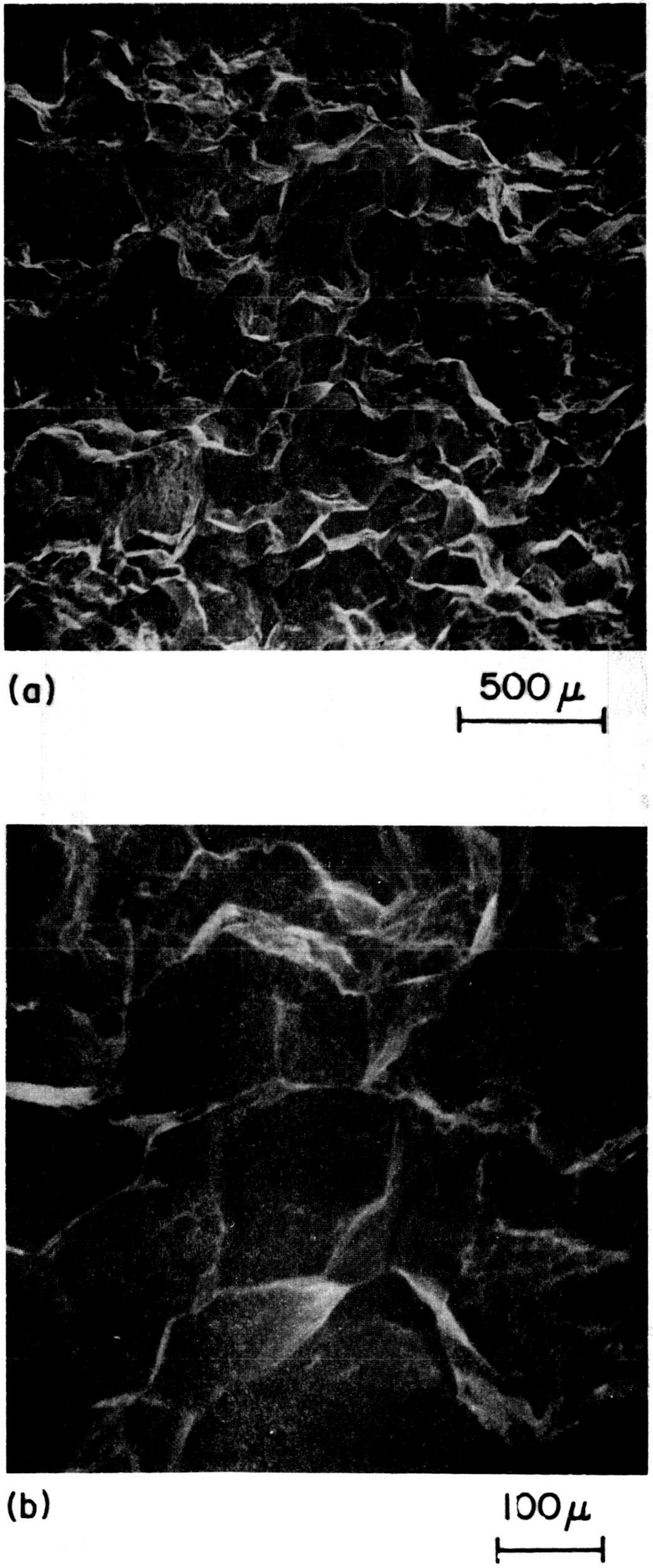

Fig. 6. - SEM micrograph of the fracture surface of the portion of a specimen failed in Stage I; (a) a low magnification, (b) high magnification.

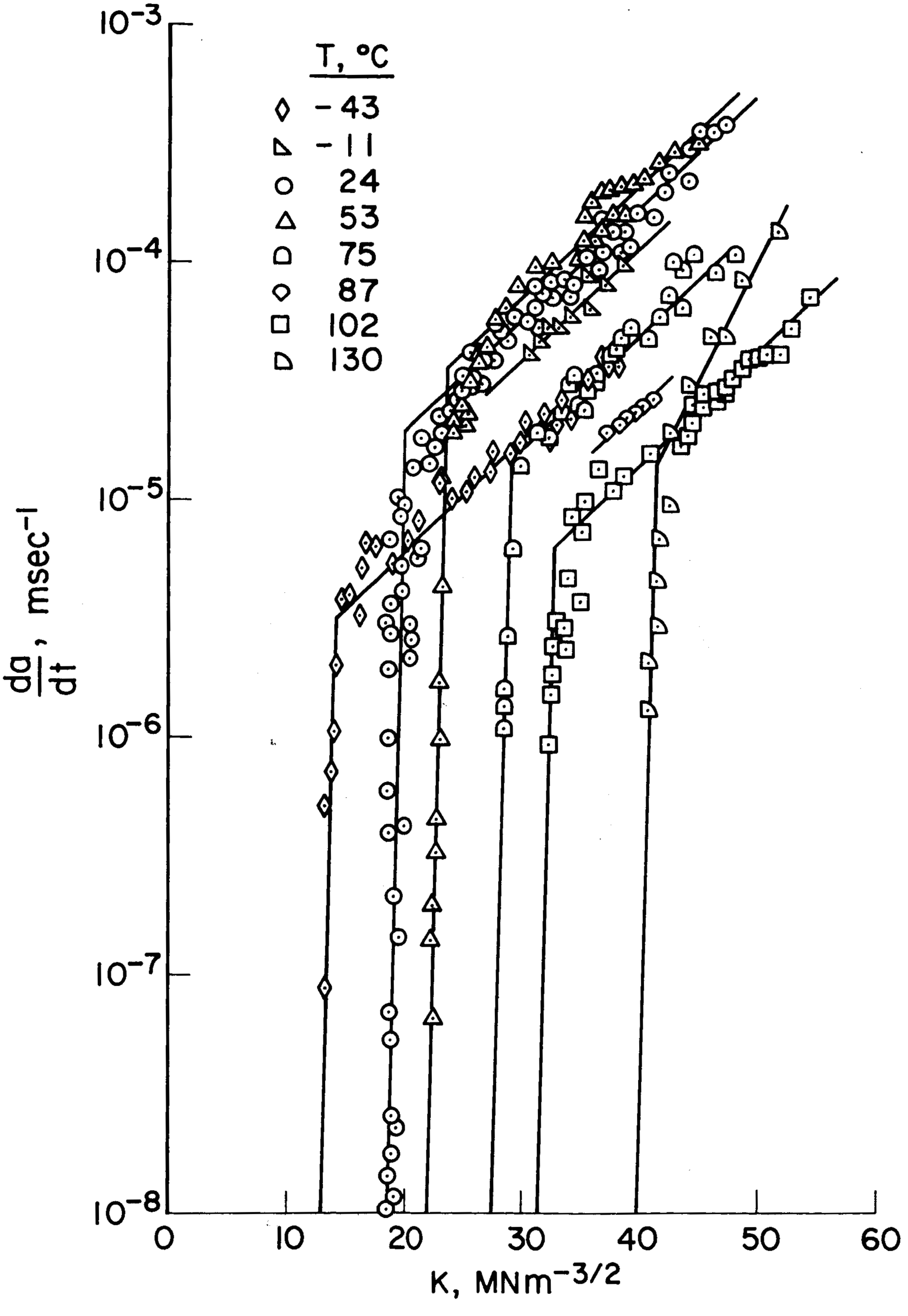

Fig. 7. - The K dependence of da/dt at various temperatures in 77.3 kN m^{-2} hydrogen for 4130 steel having a yield strength of 1330 MN m^{-2}.

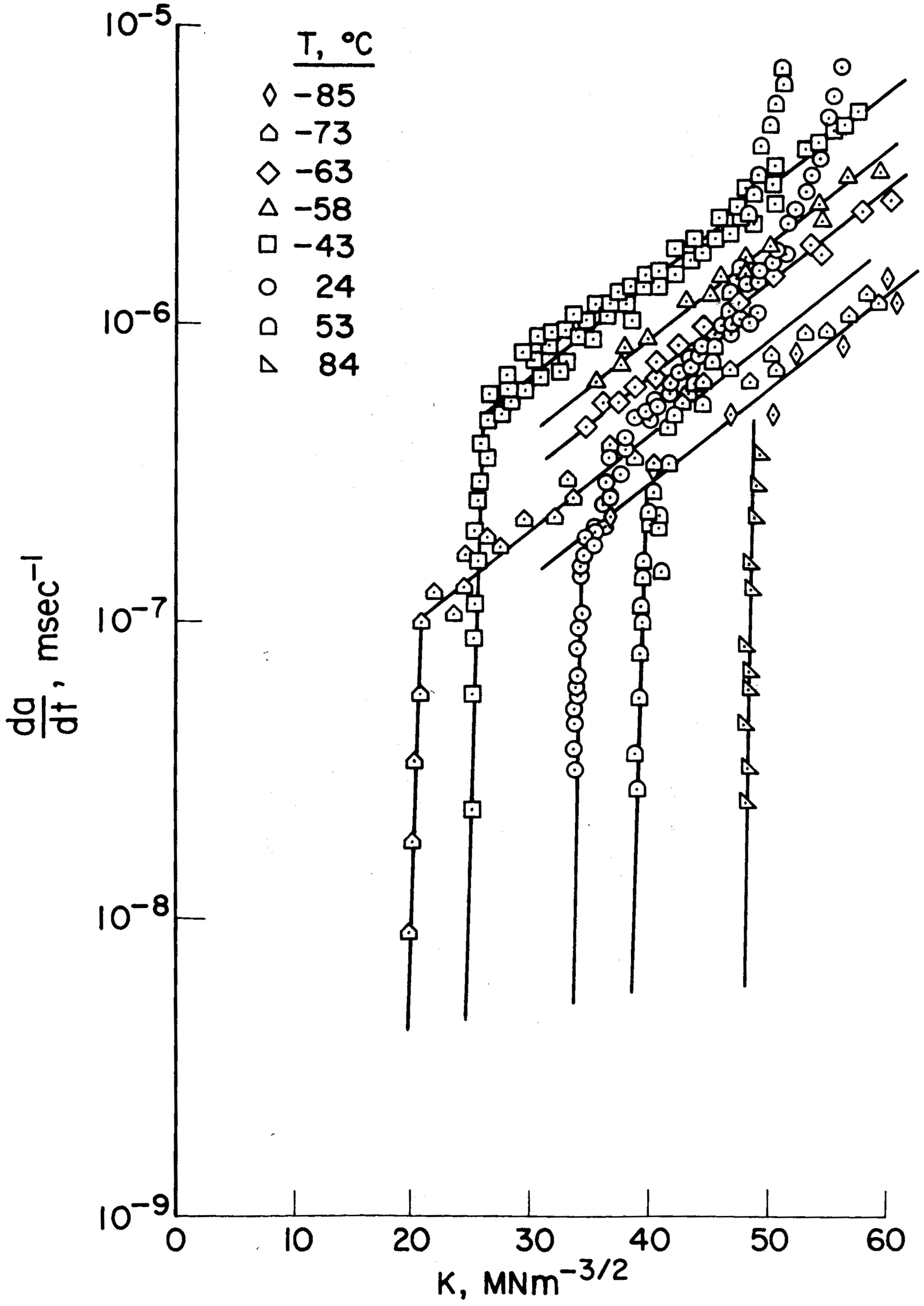

Fig. 8. - The K dependence of da/dt at various temperatures in 77.3 kN m^{-2} hydrogen for 4130 steel having a yield strength of 1190 MN m^{-2}.

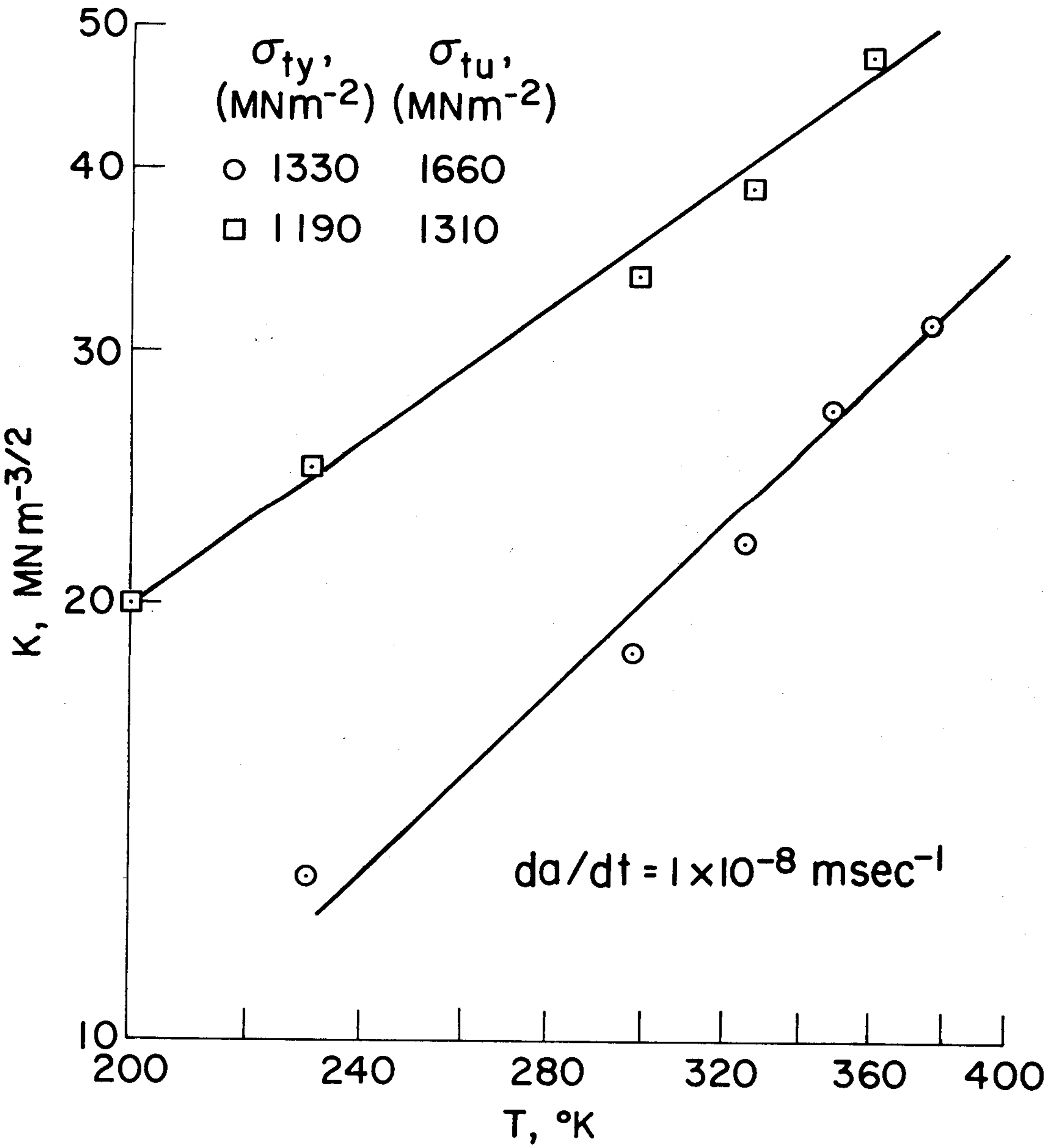

Fig. 9. - The influence of temperature on K in 77.3 kN m^{-2} hydrogen at a constant $(da/dt)_I$.

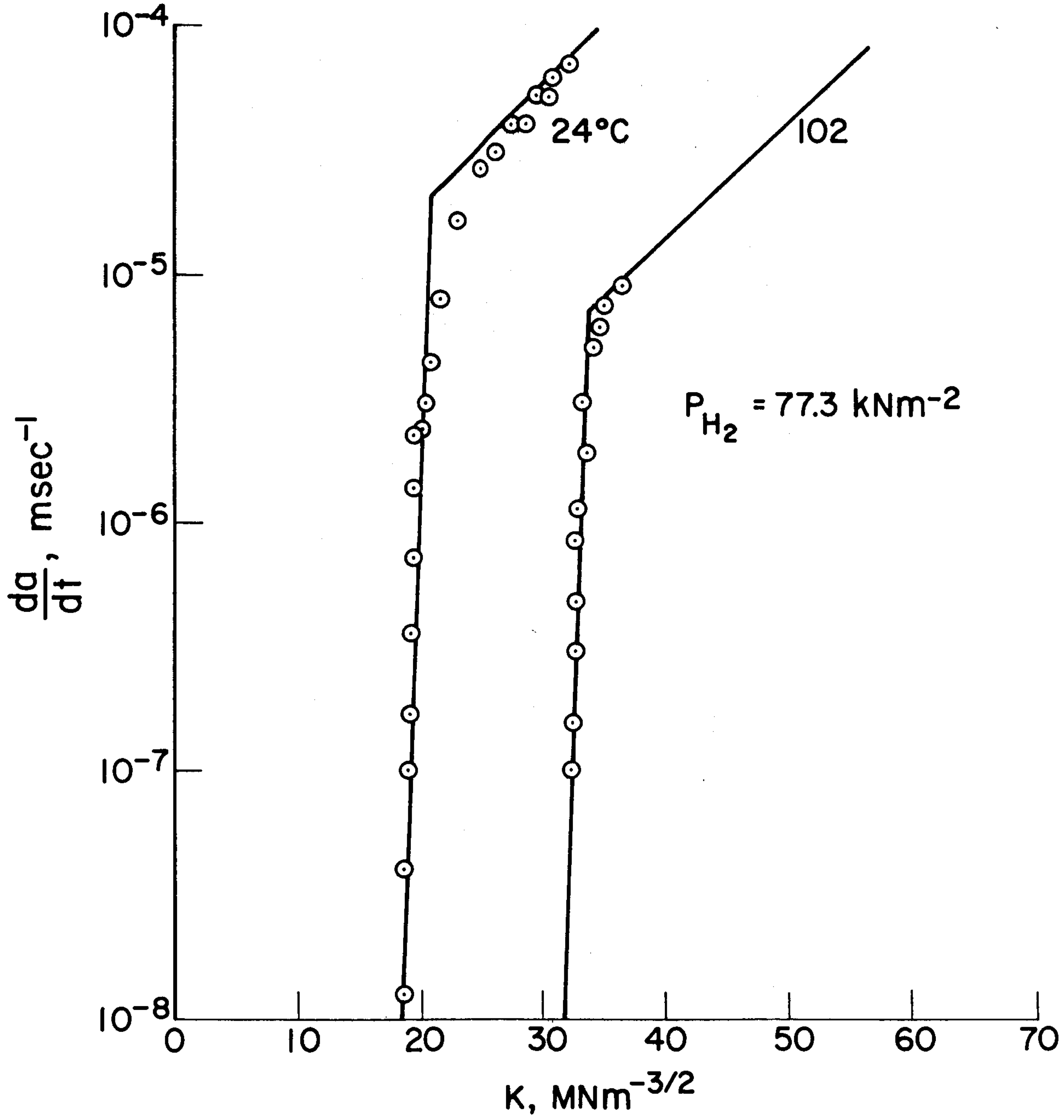

Fig. 10. - The influence of a change in temperature on Stage I crack growth in 77.3 kN m^{-2} hydrogen.

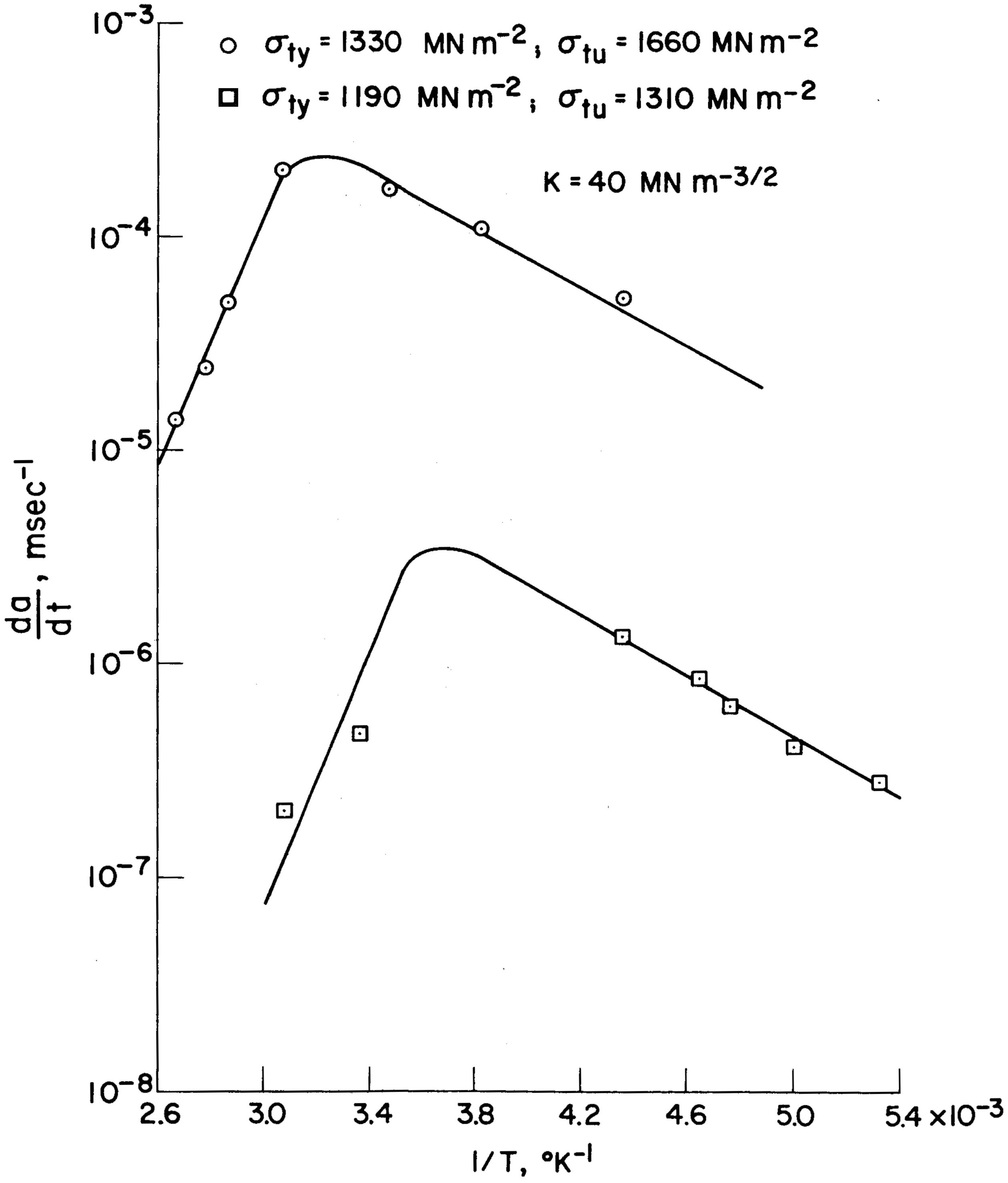

Fig. 11. - An Arrhenius plot of the temperature dependence of $(da/dt)_{II}$ at a constant K in 77.3 kN m^{-2} hydrogen for 4130 steel having yield strengths of 1330 and 1190 MN m^{-2}.

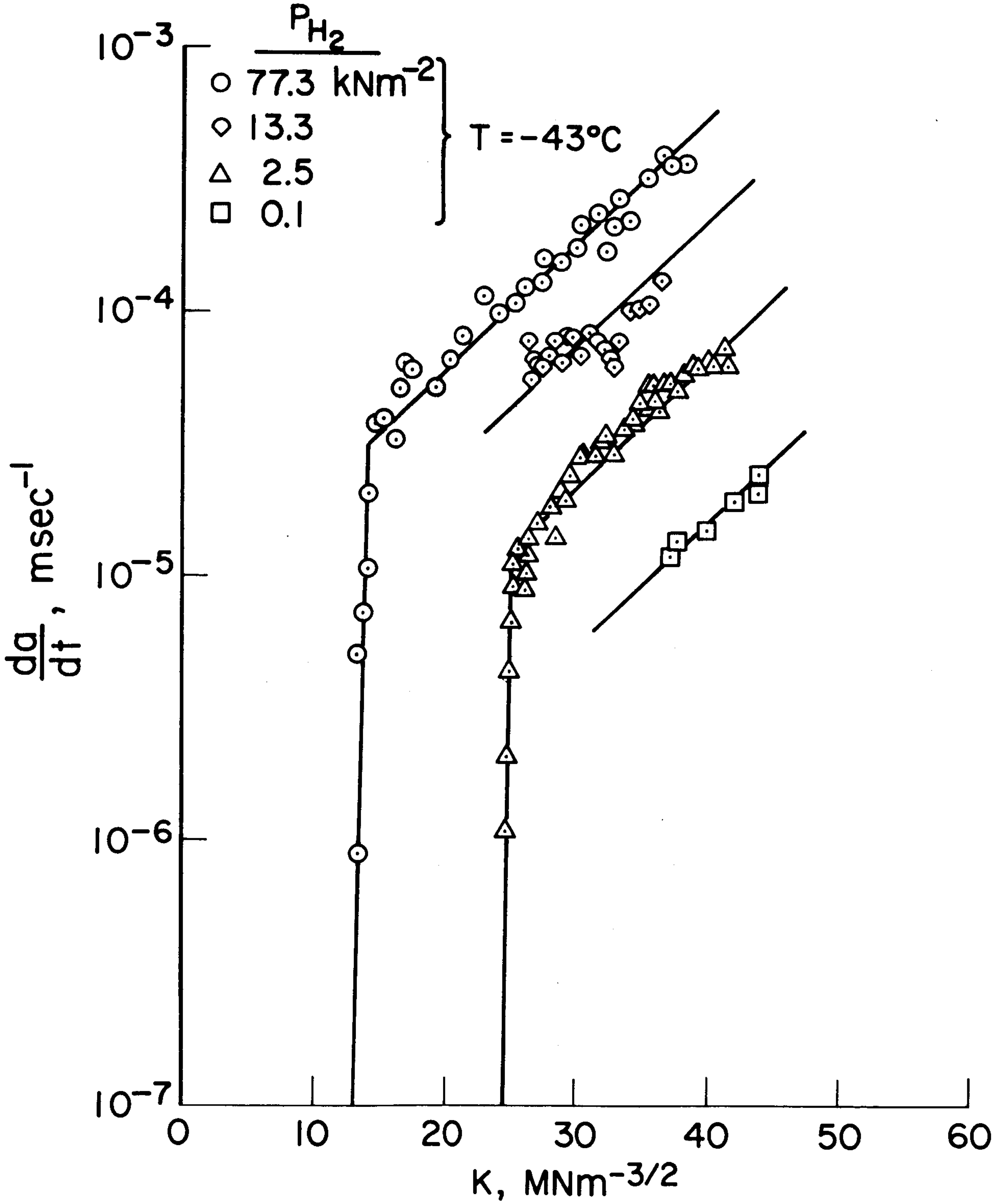

Fig. 12. - The K dependence of da/dt at various hydrogen pressures at -43°C.

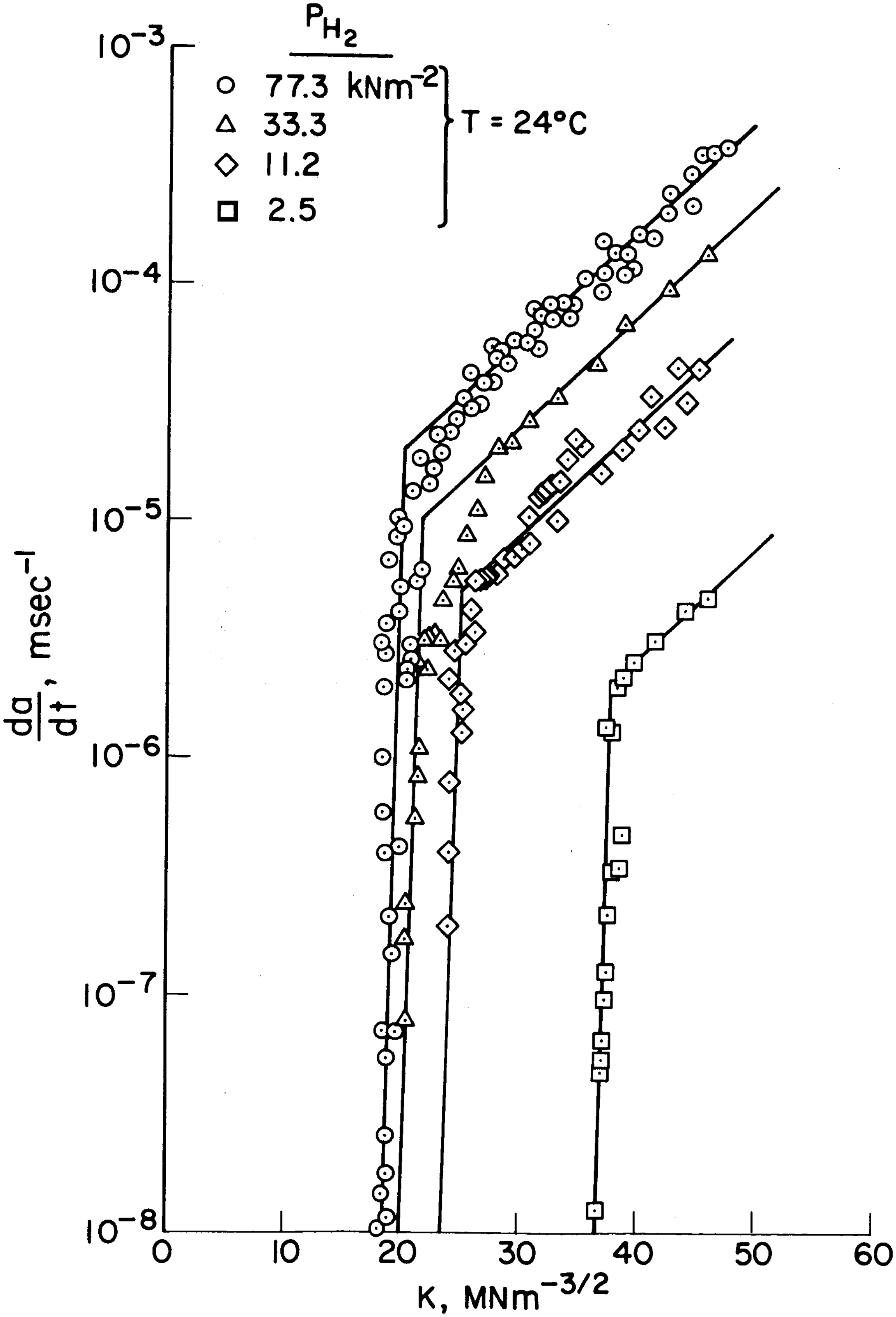

Fig. 13. - The K dependence of da/dt at various hydrogen pressures at 24°C.

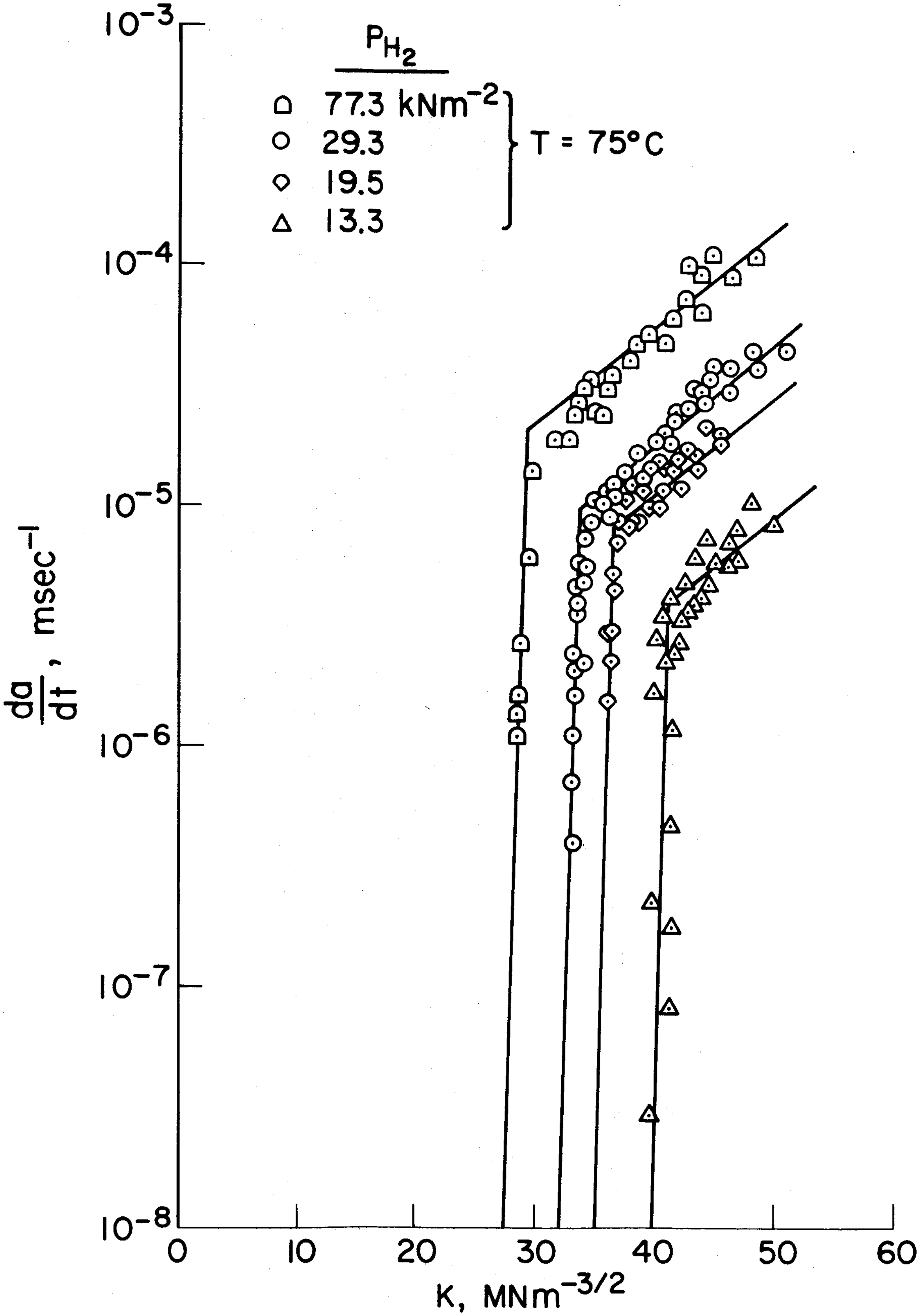

Fig. 14. - The K dependence of da/dt at various hydrogen pressures at 75°C.

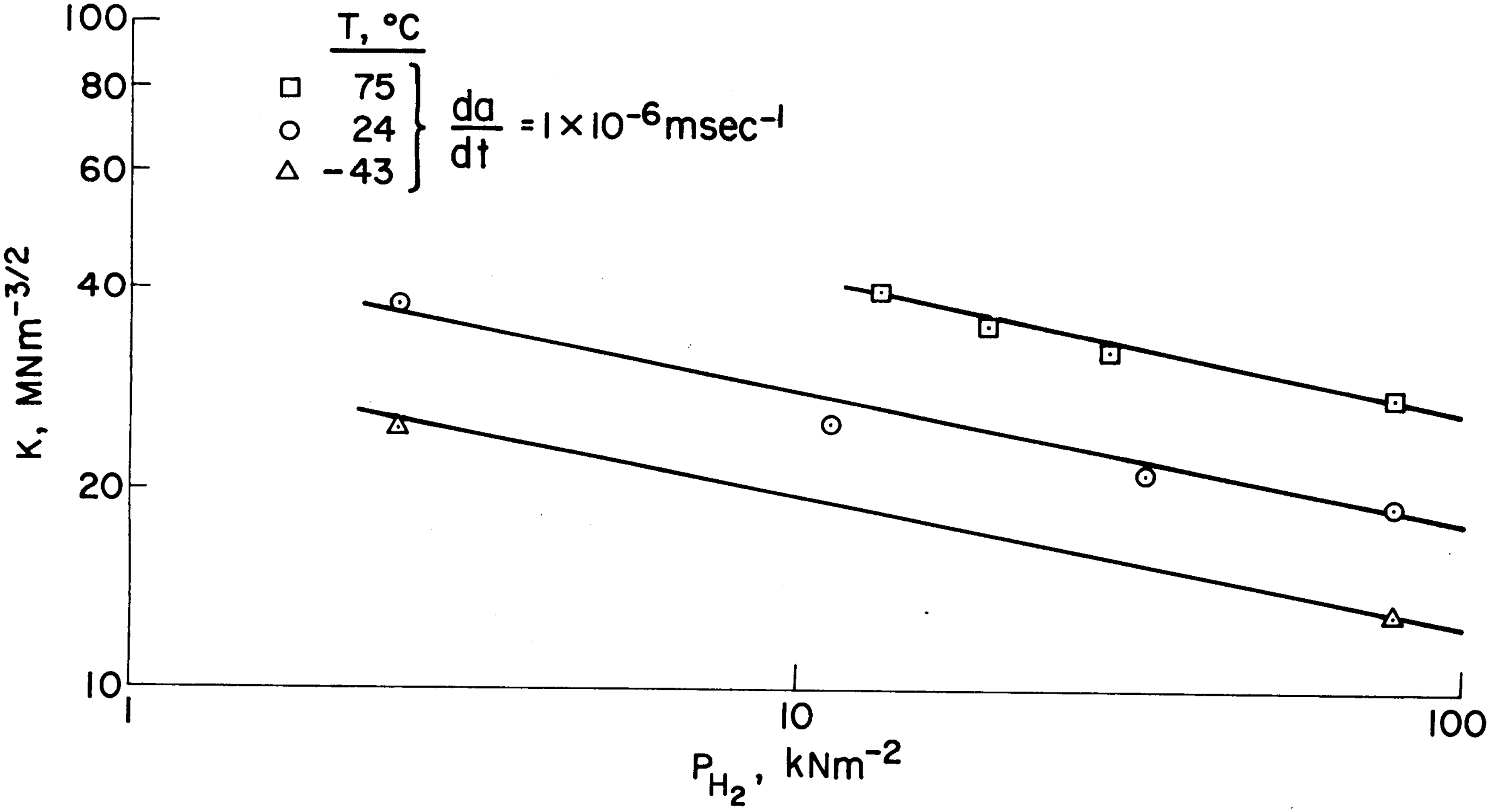

Fig. 15. - The influence of hydrogen pressure on K at a constant $(da/dt)_I$ at three temperatures.

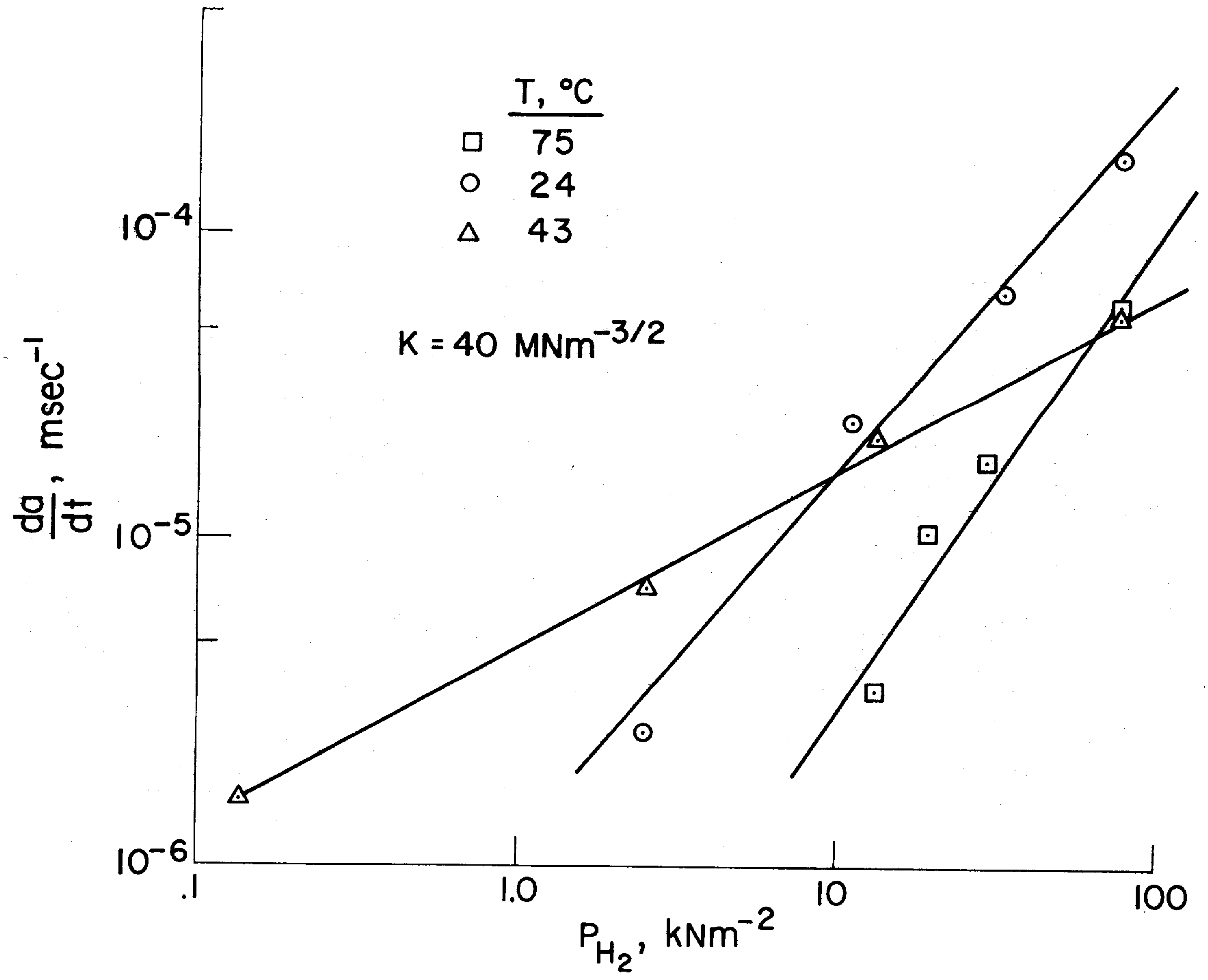

Fig. 16. - The influence of hydrogen pressure on $(da/dt)_{II}$ at a constant K at three temperatures.

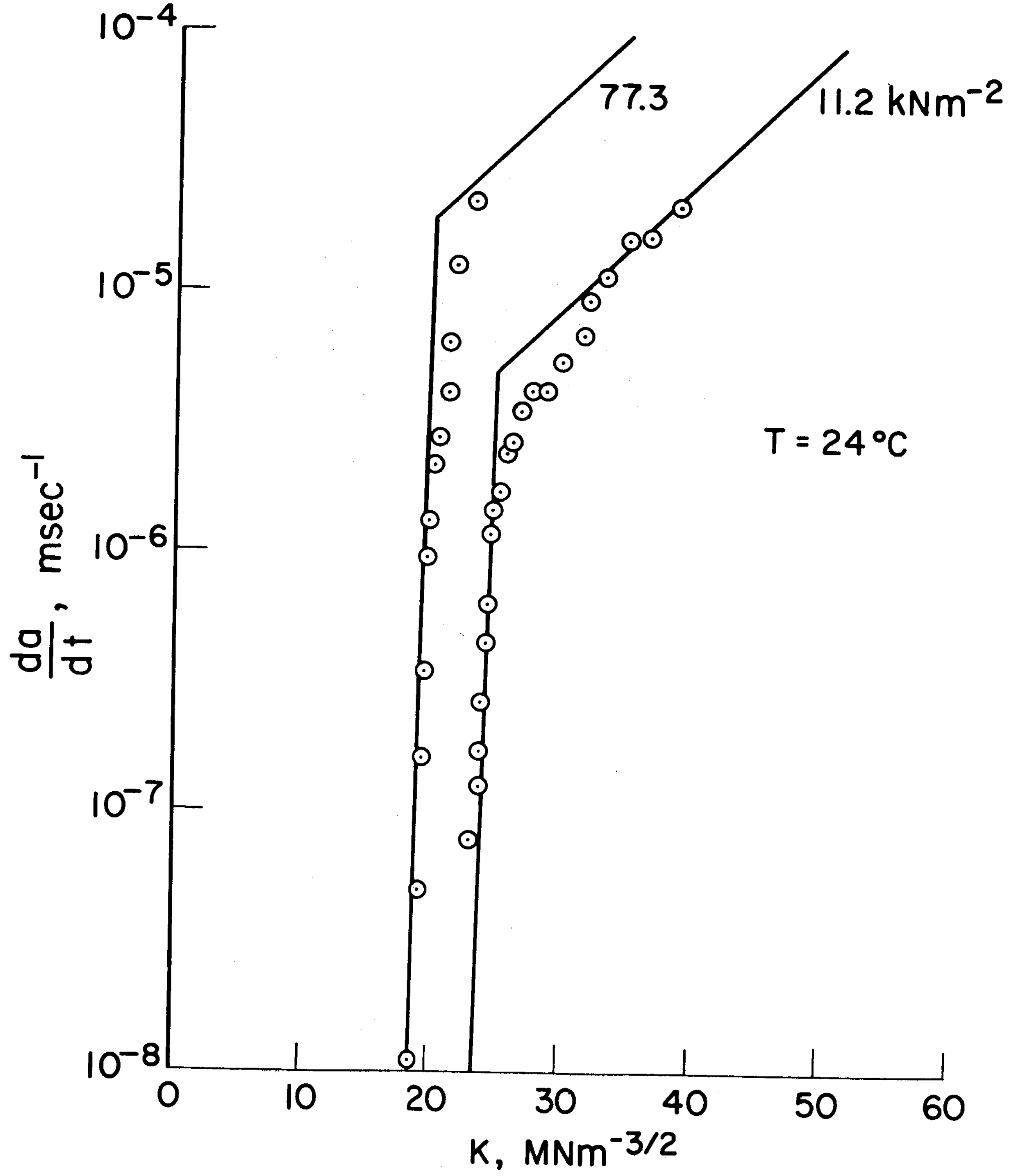

Fig. 17. - The influence of a change in hydrogen pressure on Stage I crack growth at 24°C.

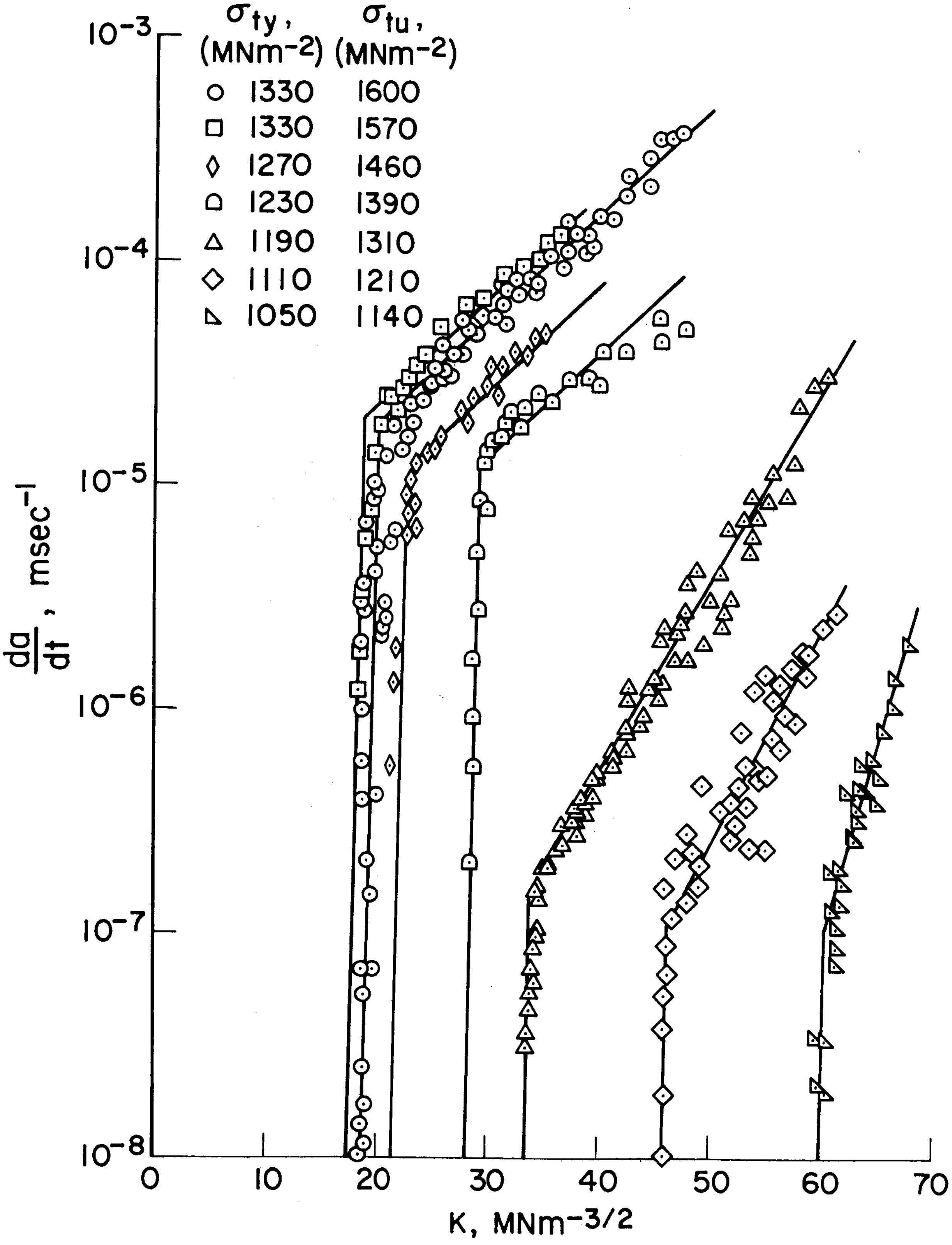

Fig. 18. - The K dependence of da/dt in 77.3 kN m^{-2} hydrogen for 4130 steel having various strength levels.

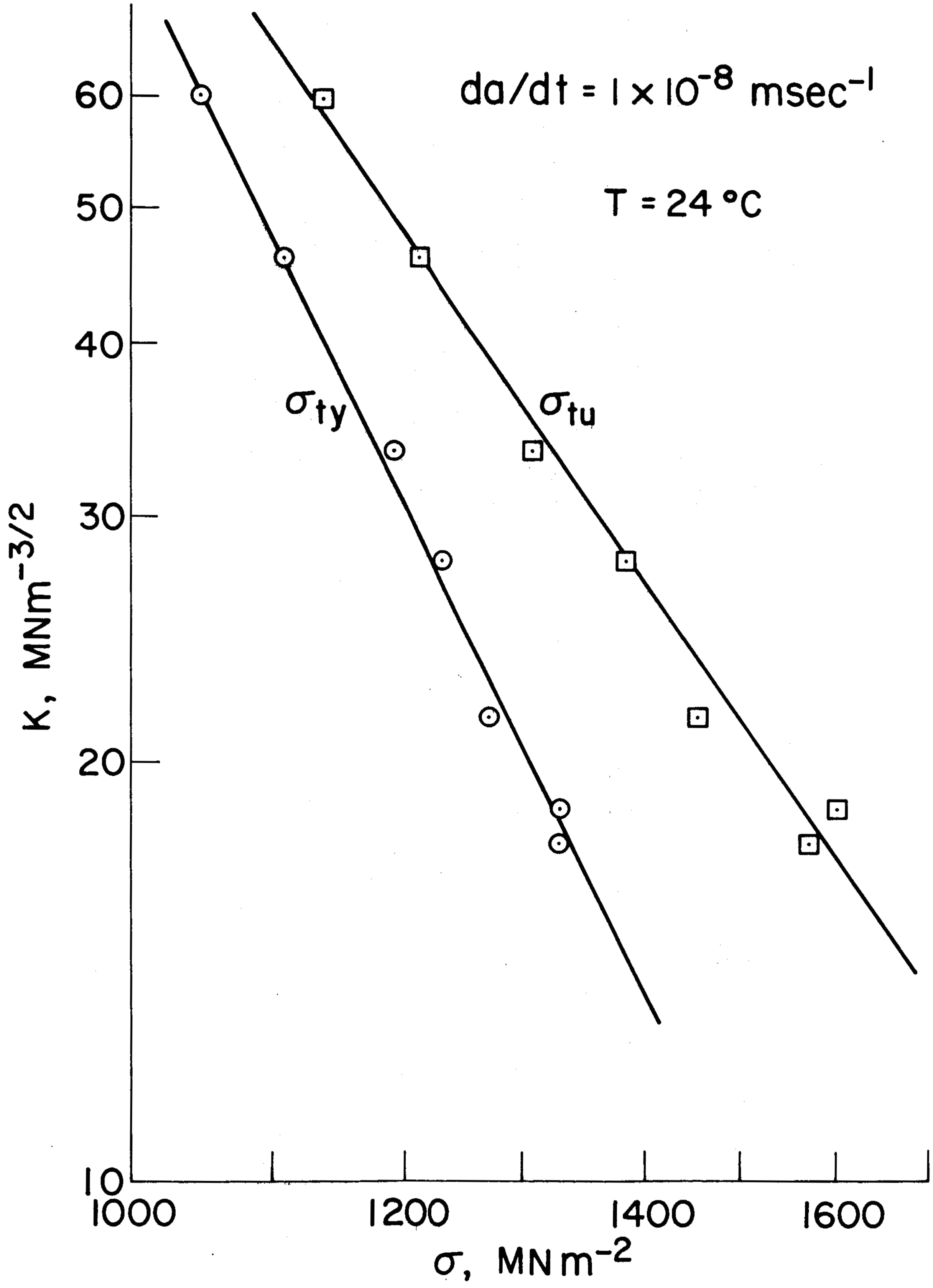

Fig. 19. - The influence of strength level on K at a constant $(da/dt)_I$ in 77.3 kN m^{-2} hydrogen at 24°C.

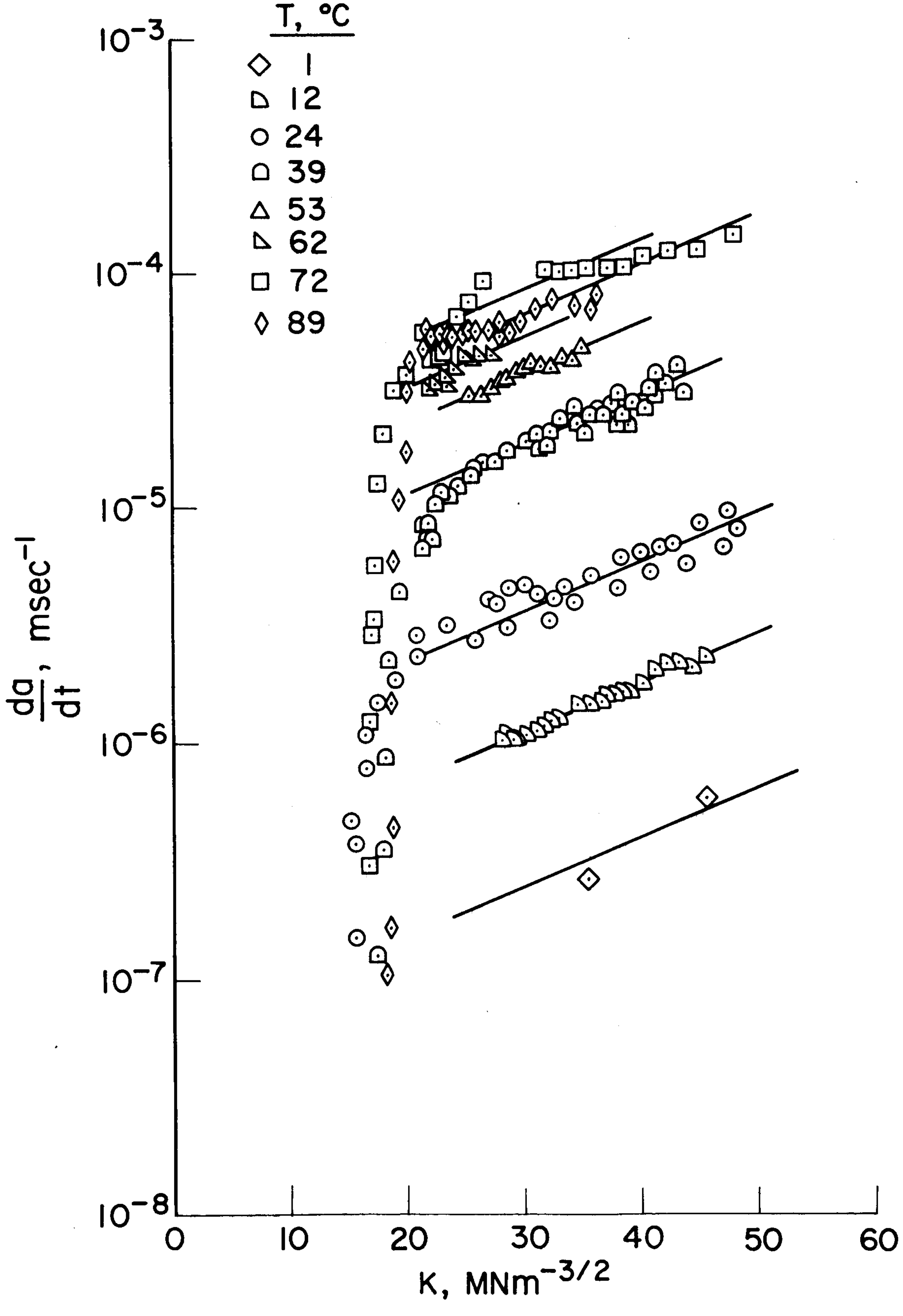

Fig. 20. - The K dependence of da/dt at various temperatures in distilled water for 4130 steel having a yield strength of 1330 MN m^{-2}.

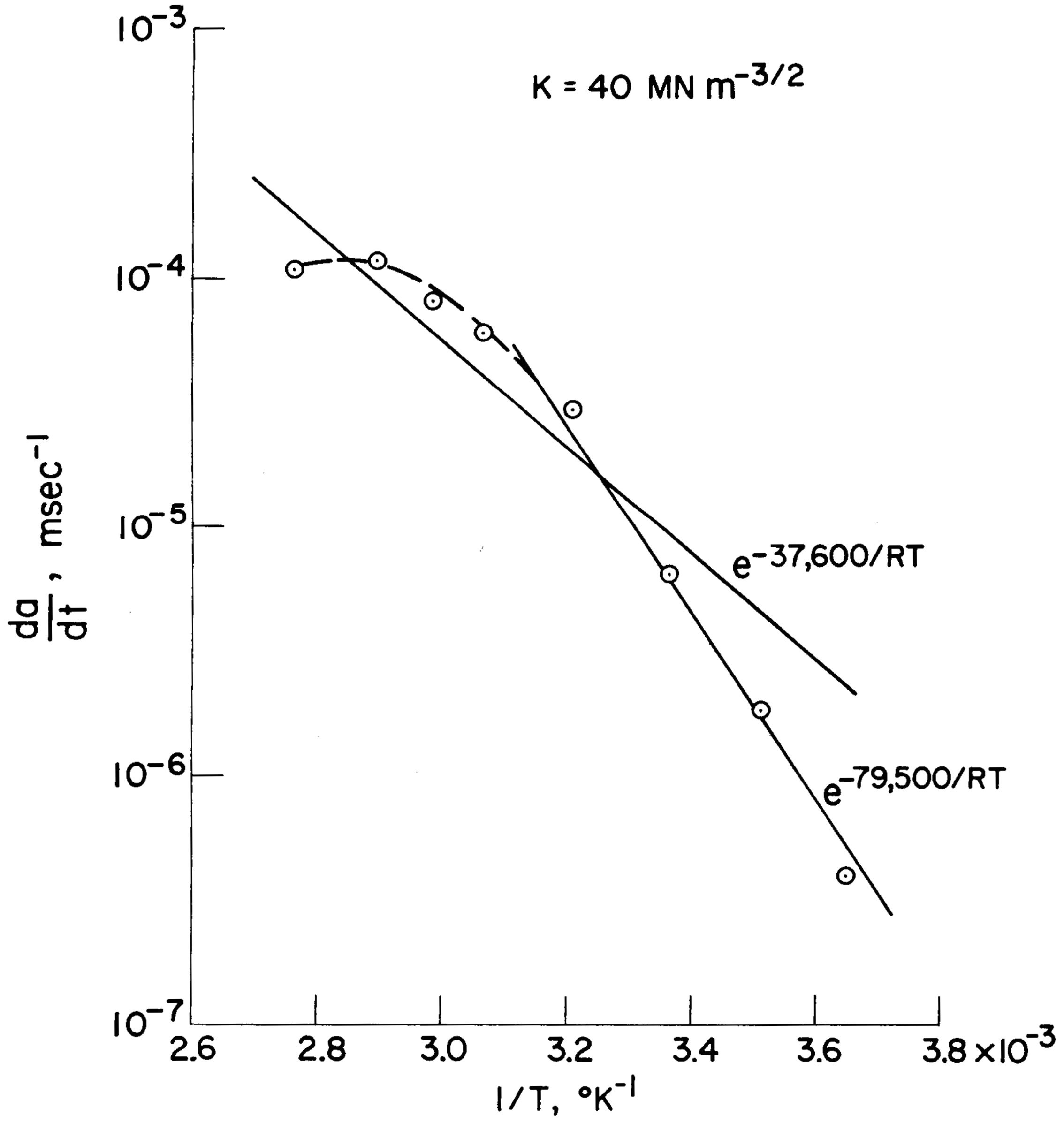

Fig. 21. - An Arrhenius plot of the temperature dependence of $(da/dt)_{II}$ at a constant K in distilled water.

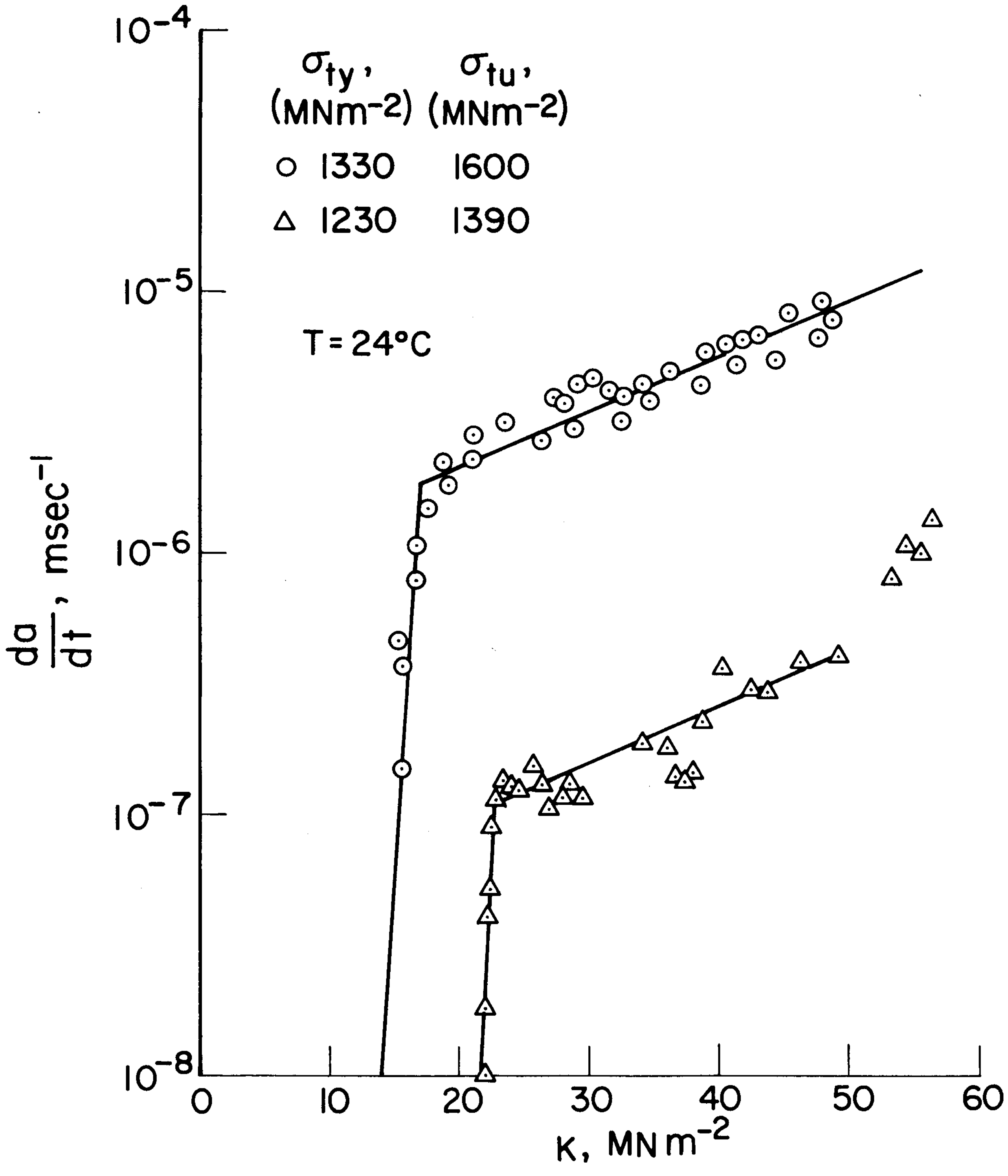

Fig. 22. - The K dependence of da/dt in distilled water at 24°C for 4130 steel having yield strengths of 1330 and 1230 MN m^{-2}.

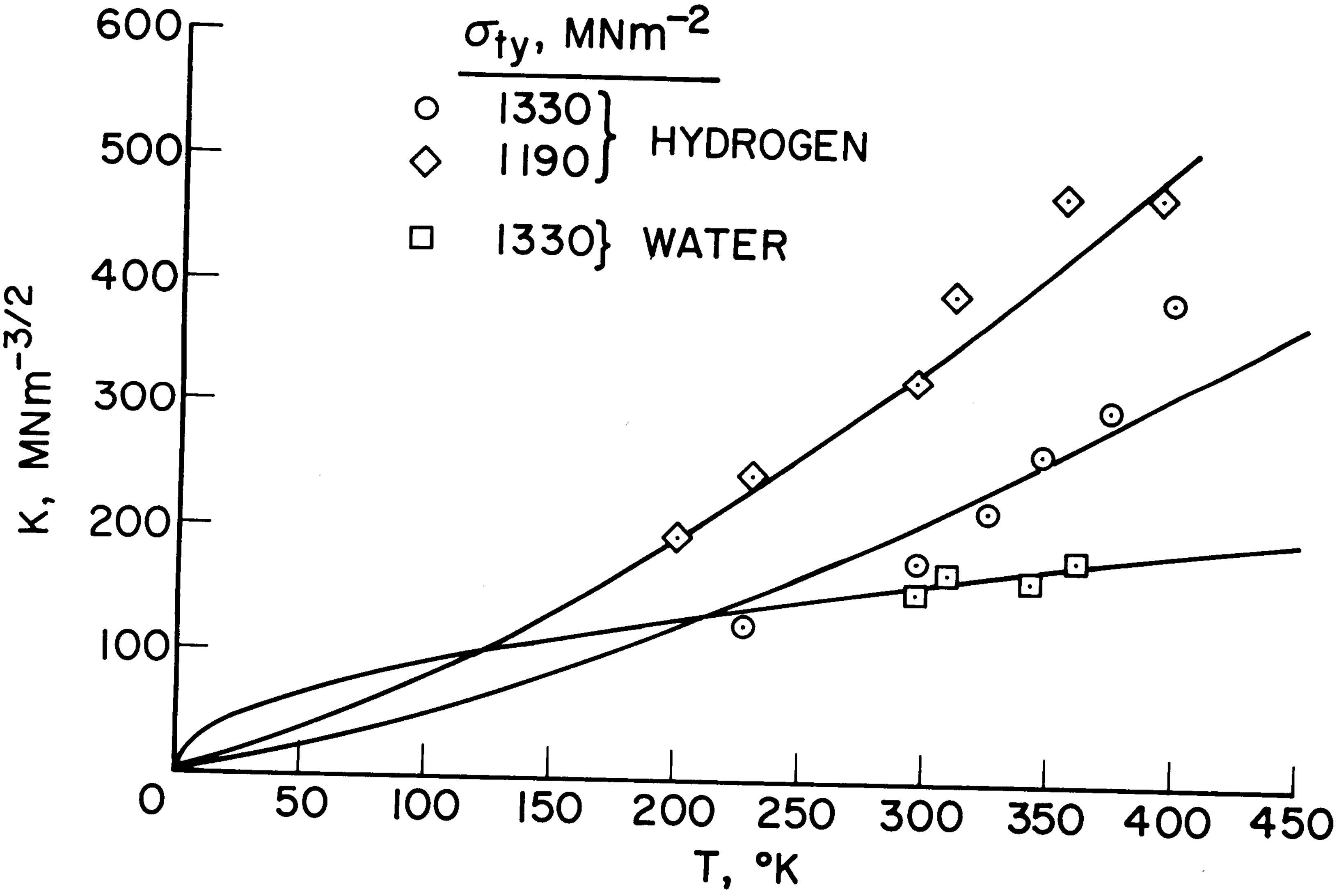

Fig. 23. - The observed and predicted influence of T on K at a constant $(da/dt)_I$ in hydrogen and in water environments.