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Hydrogen Induced Crack Growth in Grade-12 Titanium

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MASTER

KEY WORDS: Hydrogen, Crack Growth, Titanium, Nuclear Waste

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ABSTRACT

Internal hydrogen induced crack growth rates were measured in Grade-12 titanium which is a candidate material for high level nuclear waste containers. As-received and hydrogen charged samples (5 ppm to 330 ppm hydrogen) were used for slow crack growth measurements at constant loads using a Krak Gauge. The testing temperature ranged from room temperature to 148°C. The crack growth kinetics under low to moderate loads are linear, but this linear rate is interrupted by discrete fast crack jump segments with parabolic or cubic type kinetics. These fast jump segments are thought to be associated with the passage of the crack front through the alpha-beta interface phase or with the initial loading sequence. By measuring striation spacings on the fracture surface, most crack growth rates observed are found to be in stage II. The striations are considered to be associated with hydride fracture. The crack path is either transgranular in the alpha phase or interfacial in the alpha phase adjacent to the beta phase. For transgranular growth, crack growth rates are constant and slower than those for interfacial growth which is associated with fast crack growth through a high hydrogen concentration region. Most stage II crack growth rates depend slightly on the stress intensity suggesting the contribution of plastic tearing process to stage II kinetics. The activation energies for crack growth are much lower than the activation energy of hydrogen diffusion through the alpha phase, implying that hydrogen is transported along dislocations, grain boundaries or interfaces. When the temperature is increased, the crack velocity first reaches a maximum and then decreases at higher temperatures. These temperature effects come from lower hydrogen concentration trapped at dislocations or from slower hydride

nucleation kinetics, both at higher temperatures. The effects of overall hydrogen concentration and grain size are not significant within the accuracy of the tests. The present results are discussed with the potential contribution of the crack jump to overall crack propagation rates and with the correlation of surface crack and internal crack.

1. INTRODUCTION

ASTM Grade-12 titanium is a candidate material for high level nuclear waste containers in rock salt repositories.¹ Brine in the rock salt when irradiated by gamma radiation from nuclear waste will produce high pressure hydrogen.² As-received Grade-12 titanium has about 35 ppm hydrogen. Recent work by Ahm and others³ has shown that Grade-12 titanium is susceptible to internal hydrogen embrittlement for hydrogen levels in excess of the as-received level. This is considered to be caused by hydride formation at crack tips.⁴⁻⁷ For a quantitative study of the internal hydrogen embrittlement of Grade-12 titanium, slow crack growth rates are measured in this study at various conditions. The data will provide basic information necessary for the prediction of hydrogen induced delayed failure.

The slow crack growth kinetics in stage I and stage III are known to be typically strongly dependent on stress intensity, and independent of stress intensity in stage II. Sometimes stage II is known to be a function of stress intensity too, especially in internal hydrogen embrittlement.⁸ In stage I crack growth, the hydride size is greater than the plastic zone size at the crack tip and, therefore, subject to an elastic stress. On the other hand, in the stage II crack growth period, hydride is formed in the semicohesive zone inside the well developed plastic zone. The stage II hydride is subject to a plastic stress. Stage III is known to come from plastic tearing process independent of hydrogen behavior.⁸ The temperature dependence of crack velocity of hydride forming metals has been studied quantitatively.^{5,8-11} The observed activation energy for crack growth rates is usually lower than 52 KJ/mole needed for alpha phase matrix diffusion of hydrogen in titanium.

The observed low activation energies have been attributed to short circuit diffusion, most likely pipe diffusion along dislocations, or interphase or grain boundary diffusion.¹² Also, the crack velocity is often found to decrease at higher temperatures. This is thought to be connected with hydrogen solubility limits in the alloy and also hydride nucleation kinetics.¹² Stress intensity and temperature are the most important parameters determining crack growth kinetics. Hydrogen concentration and grain size are the next important parameters. Higher hydrogen concentrations and smaller grain size increase the diffusion limited kinetics¹³ as well as nucleation controlled kinetics.¹⁴

The crack jump process, as a transient effect, has been discussed in the literature particularly for stage I where the plastic zone size is comparable to or less than the grain size. Three different types of crack jump have been reported. The first was observed in hydride fracture detected by acoustic emission for Zr-2.5 Nb alloy.¹⁵ This type of crack jump is not resolved in conventional crack growth measurements. The second is associated with initial loading. Upon loading, a fresh surface would be exposed at the crack tip, thus allowing the surface reaction to begin.¹⁶ The diffusion process may go through a transient period until an equilibrium concentration of hydrogen is achieved for the stress conditions imposed. Upon reaching this equilibrium concentration, crack growth is faster than the steady state value. The third type of crack jump is associated with a second phase or a grain boundary.^{17,18} The crack velocity is either accelerated or retarded upon passing through the second phase or grain boundary. When the interphase spacing is sufficiently large compared to the plastic zone size, the crack jump is resolvable.¹⁸ It can be detected when a jump triggers further cracking in the surrounding material.¹⁷

In this study, we measure crack velocities for various stress intensities, temperatures, grain sizes and hydrogen concentrations. Both steady state and transient effects of crack propagation are considered for these variables.

2. EXPERIMENTAL PROCEDURES

Grade-12 titanium is a dilute alloy of Mo and Ni and composed of alpha phase and about 10 volume percent beta phase along grain boundaries. Nominal composition of the samples from TIMET is shown in Table 1 and the initial microstructure is shown in Figure 1. The as-received material was found to contain about 35 ppm hydrogen.

Compact tension specimens specified by ASTM¹⁹ were machined to the T-L orientation with a thickness of 17.8 mm. The specimen surface was polished to 600 grit of SiC. After cleaning with detergent, acetone, methyl alcohol and distilled water, some samples were hydrogen charged thermally. In this procedure, hydrogen at a given pressure was allowed to contact heated specimens in a vacuum furnace at 10^{-7} torr after being purified by a palladium membrane (Matheson Model 83-71). The pressure drop upon annealing at 900°C for four hours was used to calculate the hydrogen content of the sample with a known volume of the vacuum furnace. The hydrogen concentration was confirmed after mechanical testing by measuring pressure increase during vacuum degassing at 900°C and subsequent analysis with a mass spectrometer.

Thin foil Krak Gauge techniques²⁰ (Hartrun Company) were adopted for the measurement of crack growth rates. A foil gauge was attached to the sample surface by bonding glue and cured at 150°C for 2 hours. Measured potential drops at constant current were converted to crack length with a Fractomat

device (Hartrun Company). Before crack growth measurements, samples were fatigue-precracked in the tension-tension mode (35-350 Kg at 20 Hz) to obtain a sharp initial cracking. The cracks were propagated at a constant applied load using creep machines (ATS Series 2000). An environmental heating chamber was used to control the testing temperature. Initially, a very low load was applied, and this was increased gradually until an appreciable crack velocity was obtained. In each loading interval, the crack length was monitored. The testing temperature was varied from room temperature to 148°C. Some specimens were tested at one temperature while other specimens were tested at different temperature for each loading interval. For confirmation of Krak Gauge test, a direct potential measurement was performed without Krak Gauge at room temperature and input current 10A.

In this technique we measured surface crack length. Therefore, it was necessary to correlate the internal crack length, surface crack length and surface plastic zone size. The correlation was obtained by examining the fracture surface and sample surface with a scanning electron microscope (SEM). SEM works also provide information necessary to identify embrittlement mechanism.

3. RESULTS AND DISCUSSION

Table 2 shows the matrix for the conditions of slow crack growth experiments and typical crack growth kinetics are shown in Figures 2-4. In Figure 2, the sample was tested at various temperatures while samples for Figures 3 and 4 were tested at one temperature. The results show that the crack velocity is dependent on stress intensity, which is not an unusual case as discussed before. Also the measured crack velocity is nearly independent

of hydrogen concentration and grain size. Figure 5 shows an example of a failed sample and fractograph which shows fatigue zone, slow crack growth zone and fast crack growth zone. In the fatigue cracked zone, the fractograph shows mostly ductile fracture (Figure 6). On the other hand, the slow crack growth zone has ductile and cleavage fracture (Figure 7). Secondary cracking is often observed. For the fast crack growth zone, ductile fracture is dominant with a significant amount of secondary cracking (Figure 8). The secondary cracking is considered to be associated with the interface separation.³

Before we present and discuss the crack growth kinetics for various test conditions, it is necessary to describe the way the crack growth kinetics were measured. Typically for extended test times, two types of crack growth rate curves are observed as shown in Figure 9 and Figure 10. In Figure 9 for the beginning of crack growth, the crack moves at slow (close to linear) rates separated by short intervals in which the crack propagates very rapidly. This fast crack growth occurs during a constant load period or immediately after the load is increased. The accelerating growth rate section of the curve in the Figure 10 precedes sample fracture.

In the present measurements, we separated the slow growth rates and the jump rates in the curve of crack length versus time. The slow growth rates are obtained from slow rates separated by the short intervals while the jump rates are calculated from the initial slope of the jump. Crack jump mechanisms have been reported in the literature for other similar materials.¹⁶⁻¹⁸ Landes¹⁶ has postulated that the crack jump upon loading is associated with a transient period until an equilibrium concentration of hydrogen at crack tip is established. Typically, the equilibrium hydrogen concentration at crack tip is

lower than the initial hydrogen concentration. This leads to a crack jump during this transient period when the hydrogen level at the crack tip is high. Akhurst and others¹⁷ and Antolovich and others¹⁸ believe that the crack jump is associated with a second phase or with a region of high hydrogen concentration such as grain boundaries. The second phase is holding the crack to a certain time and, then, the crack jump occurs when the second phase no longer hold the crack.¹⁸ In the present study, we propose that the crack jump is associated with either (1) loading increases and (2) the passage of the crack front through the alpha-beta interface phase, as shown in schematically Figure 11. In Figure 11, the zigzagged line A shows that the crack path is either transgranular (Regions 1 and 3) in the alpha phase (white grain) or interfacial (Region 2) in the alpha phase adjacent to the beta phase (black area). For transgranular growth, crack growth rates (Regions 1 and 3) are steady and slower than those for interfacial growth which is associated with a crack jump (Region 2) because of a high hydrogen concentration in this region.³ Two kinds of observed phenomena support this proposal. First the crack jump step shown in Figure 9 reflect that the crack jump can be associated with several grains because the high hydrogen concentration regions are interconnected with the beta phase³ and grain boundaries.²¹ Once the microcrack at the crack front nucleates and initiates the increment of crack advance, it tends to trigger further cracking in the surrounding material.¹⁷ Secondly, such cracking is shown in Figure 7 as a cleavage zone. The cleavage width is comparable to the crack jump height shown in Figure 9. In this work, we have measured crack growth rates on the specimen surface. It is known that there is a linear relation between plastic zone growth rates (with the appearance of

secondary cracks) and surface crack growth rates.²² Typically, the Fractomat reading indicates the secondary cracking. Also, the growth of the surface plastic zone and the appearance of secondary cracks can be due to the advance of an internal crack that tunnels far ahead in the near free surface layer.²² This is particularly true for stage II where crack growth rates are rather independent of stress intensity, which leads to a correlation between the crack growth rates for plane strain condition (tunnel effect) and the crack growth rates for the plane stress condition (surface effect). Therefore, a one to one correlation between Fractomat reading and the internal crack growth rates is not unrealistic. We used the direct potential method also and found such jump on loading (Figure 12) and small jump associated with crack passage through the beta phase or grain boundary (Figure 13). The latter jump is less distinctive simply because it is a result of statistical averaging over the entire crack front compared to the surface crack growth rates from the Fractomat reading. For the study of the internal crack front, a direct potential method is not necessarily desirable because it averages crack growth behavior over the entire sample thickness without distinguishing the surface crack from the internal crack.

There is also a second type of crack jump associated with hydride fracture.^{4-7,15} In this hydride fracture, the hydrides are formed at crack tips and are considered to be fractured instantaneously once fracture initiates. Since the hydride size is typically small,²³ it is very difficult to detect hydride formation and the subsequent fracture by conventional methods. Acoustic emission is a method to monitor hydride fracture.¹⁵ Typically the hydride fracture leads to a striation on the fracture surface. Figure 14 shows

such striations observed on the fracture surface of as-received Grade-12 titanium. The hydride size determines stage I and stage II crack propagation behavior. When the hydride size is greater than plastic zone size, hydride is subject to elastic stress (stage I). On the other hand, plastic stresses will be present when the plastic zone size is greater than the hydride size (stage II).⁸

Figures 2 to 4 are examples of crack growth kinetics for various experimental conditions. Solid circles are measured kinetics obtained by excluding the observed fast crack jump increments in the Fractomat readings. This leads to relatively low crack growth rates. Information on the crack jump are shown in Figures 2 to 4 as open circles which represent the initial crack growth rates in a jump. Typically, these values are greater than steady state values because cracks propagate in high hydrogen concentration sites such as grain boundaries²¹ or the beta phase.³ In these measurements it is very difficult to determine whether crack growth is in stage I or in stage II since stage II type plateaus are rarely observed. However, since the striation spacing on the fracture surface is much smaller than plastic zone size, we can assume most of the kinetics are relevant to stage II. The absence of plateaus may be explained with the help of fractographic data. As we see in Figure 7, the cleavage regions are accompanied by ductile regions, which indicates that both stage II and stage III (ductile tearing process) processes contribute to the observed crack growth rates. Even though crack jump increments are often observed in stage I, stage II is also reported to show much jump sometimes¹⁷ as is the case here.

The effect of hydrogen concentration level was also examined for samples with the same microstructure tested at various temperatures and stress intensities. No effect of hydrogen concentration level was found within the accuracy of the tests since the crack velocity data all fell within a scatter band. This can be explained in the case of slow linear crack growth through the alpha phase since the hydrogen in this region is probably at or close to the solubility limit of hydrogen for the alpha phase for all specimens. The remainder of the hydrogen will be concentrated in the beta regions. It is known that the solubility limit for hydrogen is several thousands of times greater in the beta phase compared to the alpha phase.³ Distinctive differences were not observed either for grain size variations. Sample Number 1-10 in Table 2 has a larger grain size as shown in Figure 15 than the grain size of an as-received sample as shown in Figure 1. Again we are measuring the crack growth kinetics only in the alpha phase, therefore the grain size may have not affected the steady state crack growth kinetics.

Figures 16 to 19 give the temperature dependence of crack velocity obtained from the data in Table 2. The stress intensity ranges in each figure were fixed to be $20 \text{ MPa}\sqrt{\text{m}}$ which is small enough to minimize scatter in the data. The triangles are for Sample 1-10 in Table 2, solid circles are for Samples 11-16 in Table 2 and open circles are for transient velocities. As expected, a maximum is observed in each curve. This maximum is attributed to a change in the mechanism for hydrogen embrittlement. Probably, at lower temperatures, the hydrogen diffusion is a controlling parameter while the high temperature curves are controlled by a precipitation process; namely, hydride formation.³ Alternatively, if fast diffusion, such as, diffusion of

hydrogen along dislocations, is rate controlling at lower temperature, the binding energy term of hydrogen to dislocations may be the cause of the maximum crack velocity observed. As the temperature is increased, the hydrogen concentration around dislocations is decreased resulting in slower crack growth rates. Although there is a significant scatter in the data, the activation energy for each curve is lower than 52 KJ/mole needed for alpha phase matrix diffusion of hydrogen,²⁴ supporting the hypothesis of fast diffusion of hydrogen along dislocations.

Table 2 shows the transient period of crack growth rates to steady state values. Although the present technique does not allow the accurate measurement of the transient period, we find generally it becomes longer as hydrogen concentration and grain size are increased. As the hydrogen concentration is increased, the transient period becomes longer because there is a larger distance of hydrogen concentration gradient from the grain boundary or second phase;²¹ therefore, it takes more time to reach steady state crack velocity. Likewise when the grain size is bigger, the concentration gradient becomes longer.²¹

In this work we find that it is very ambiguous to define the crack front equivalent to the ideal straight crack front used for linear elastic fracture mechanics. Such definition should be studied further. Also the correlation method is necessary to be explored among surface crack, internal crack, crack initiation point and stress intensity. Finally acoustic emission technique is recommended to be used extensively for more quantitative informations. Acoustic emission is a method to detect the crack jump process both from hydride fracture or from interphase fracture.

4. CONCLUSIONS

Internal hydrogen-induced crack growth rates were measured in Grade-12 titanium at constant applied loads. The average hydrogen concentration was varied from 5 ppm to 330 ppm and the testing temperatures ranged from room temperature to 148°C. Two types of crack propagation jump were observed, namely, (1) that associated with hydride fracture resulting in striation formation on fracture surface and (2) that associated with the passage of the crack front through the alpha-beta interface phase or upon initial loading. Measured striation spacings show that most crack growth rates observed are in stage II and that the crack path is either transgranular in the alpha phase or interfacial in the alpha phase adjacent to the beta phase. For transgranular crack growth, crack growth rates are steadier and slower than those for interfacial crack growth rates. The contribution of a plastic tearing process is significant in stage II kinetics. Since the activation energies for transgranular crack growth rates are much lower than the activation energy of hydrogen diffusion through the alpha phase, it implies that hydrogen transport occurs along dislocations, grain boundaries or interfaces.

As the temperature is increased, the crack velocity reaches a maximum and then decreases as the temperature is raised further. This decreased crack growth rate is considered to be from low hydrogen concentration around dislocations or from slower hydride nucleation kinetics. The effects of hydrogen concentration and grain size were not significant.

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Table 1. Nominal composition of Grade-12 titanium (weight percent).

Ni	Mo	Fe	C	H	N	O	Ti
0.80	0.30	0.3M	0.1M	0.015M	0.03M	0.25M	Balance

M denotes the maximum.

Table 2. Matrix for the conditions of slow crack growth experiments, of Grade-12 titanium

Sample Number	Hydrogen Concentration (ppm)	Temperature (°C)	Stress Intensity (MPa m)	Transient Periods (Seconds)
1	90	Room Temperature	18-82	300-2300
3	130	Room Temperature	30-75	150-3000
4	330	92-94	8-160	500-2100
5	330	Room Temperature	29-99	50-2000
7	Vacuum-annealed ⁺	92-93	8-150	20-300
8	Vacuum-annealed	Room Temperature	27-125	0-100
		52-54	36-164	0-300
		61-63	125-146	100-250
		73-75	158-212	0-200
9	35	61	72-75	200
		78	55-61	50-100
		101	44-50	0-100
		123-125	20-35	50-200
10	35	40	92-94	50-150
		60	74	400-450
		80-82	27-78	50-1500
		102	52-58	50-250
11	As-received ⁺⁺	48	17-36	0-100
		75	72-75	0-50
		95	61-66	0-100
		108-116	46-54	0-50
		130	36-41	0-150
12	As-received	78	30-53	0-100
		100	69	0-100
		120	35-50	0-50
		148	41-66	50-200
13	As-received	Room Temperature	35-69	50-100
		40	70-82	50-200
		60	80-81	50-200
		80	75-88	50-150
14	As-received	81	88-106	50-100
		100	88-96	50-150
		120	49-68	
15	As-received	Room Temperature	58-95	50-100
16	As-received	50	43-96	50-150

⁺ Vacuum annealed sample has 5 ppm hydrogen.

⁺⁺ As-received sample has 30-35 ppm hydrogen.

50 μ

Figure 1. Microstructure of alpha and beta phases of Grade-12 titanium. The beta phase is the black area along grain boundaries.

Figure 2. Crack growth kinetics of as-received Grade-12 titanium sample measured at various temperatures (sample number 11). The open circles represent transient state velocity while solid circles show steady state velocity. The number in each point is test temperature ($^{\circ}\text{C}$).

Figure 3. Crack growth kinetics of as-received Grade-12 titanium sample measured at room temperature (sample number 15). The open circles represent transient state velocity while solid circles show steady state velocity

Figure 4. Crack growth kinetics of as-received Grade-12 titanium sample measured at 50°C (sample number 16). The open circles represent transient state velocity while solid circles show steady state velocity

Figure 5. Broken sample of Grade-12 titanium and fractograph showing fatigue zone, slow crack growth zone and fast crack growth zone (Sample Number 7).

Figure 6. Typical ductile fracture surface of vacuum annealed Grade-12 titanium observed in fatigue cracked zone (Sample Number 8).

Figure 7. Typical embrittled fracture surface of vacuum annealed Grade-12 titanium observed in slow crack growth zone (Sample Number 8). Both cleavage and ductile features are observed.

10 μm

10 μm

Figure 8. Typical fracture surface of hydrogenated Grade-12 titanium observed in fast crack growth zone (Sample Number 1). Ductile feature and secondary cracking are observed. Lower micrograph shows secondary cracking and interface serrations (arrow)

Figure 9. Crack length versus time curve observed in the beginning of crack growth for extended times from Fractomat reading. This curve is from the test on an as-received Grade-12 titanium sample at room temperature.

Figure 10. Crack length versus time curve observed in the final stage of crack growth from Fractomat reading. This curve is from the test on as-received Grade-12 titanium sample at 50°C.

Figure 11. A schematic of crack growth behavior as the crack front passes through the alpha and beta regions. White grain is alpha phase and black grain is beta phase. The zigzagged line A shows the transgranular crack path (regions 1 and 3) in the alpha phase or interfacial crack path (region 2).

Figure 12. Crack length versus time curve of as-received Grade-12 titanium observed in the beginning of crack growth from direct potential method (K is 15-20 $\text{MPa}\sqrt{\text{m}}$). Crack jumps are observed. (This Figure is equivalent to Figure 9.)

Figure 13. Crack length versus time curve of as-received Grade-12 titanium observed in the final stage of crack growth from direct potential method (K is $15-20 \text{ MPa}\sqrt{\text{m}}$). (This Figure is equivalent to Figure 10.)

Figure 14. Striations observed in the fracture surface of as-received Grade-12 titanium tested at various temperatures (Sample Number 11). The upper view is an enlargement of a flat region in the lower picture.

Figure 15. Microstructure of alpha and beta phases of Grade-12 titanium after annealing in the vacuum for four hours. The beta phase is the black area along grain boundaries. When hydrogen is added the grain size tends to be bigger.

Figure 16. The measured slow crack growth rates of as-received and annealed Grade-12 titanium at various temperatures for $K = 20-40 \text{ MPa}\sqrt{\text{m}}$. Triangles are for Samples 1-10, solid circles are for Samples 11-16, and open circles are for transient velocities.

Figure 17. The measured slow crack growth rates of as-received and annealed Grade-12 titanium at various temperatures for $K = 40-60 \text{ MPa}\sqrt{\text{m}}$. Triangles are for Samples 1-10, solid circles are for Samples 11-16, and open circles are for transient velocities.

Figure 18. The measured slow crack growth rates of as-received and annealed Grade-12 titanium at various temperatures for $K = 60-80 \text{ MPa}\sqrt{m}$. Triangles are for Samples 1-10, solid circles are for Samples 11-16, and open circles are for transient velocities.

Figure 19. The measured slow crack growth rates of as-received and annealed Grade-12 titanium at various temperatures for $K = 80-100 \text{ MPa}\sqrt{\text{m}}$. Triangles are for Samples 1-10, solid circles are for Samples 11-16, and open circles are for transient velocities.