FRACTOGRAPHIC ASPECTS OF STRESS CORROSION FAILURE OF ZIRCALOY-2 IN CH_3OH/HCL SOLUTIONS

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Abstract Fracture surface of Zircaloy-2 specimens tested under constant crosshead speed in $CH_3OH/0.4$ Vol. %HCl solution with and without selenium (25 ppm) addition was studied . Using a combined process of deformation and annealing, coarse grained material was also obtained and examined. Two modes of stress corrosion crack propagation were observed: an intergranular zone caused by stress assisted anodic dissolution, and a transgranular cleavage zone, due to hydrogen absorption.

چکیده در این مقاله سطح مقطع شکست خوردگی تنشی نمونه های زیر کالوی - ۲ در محلول الکل متیلیك حاوی ۰/۴ درصد حجمی اسید کلریدریك مورد مطالعه قرار گرفت. همچنین اثر اضافه شدن ۲۵ppm سلنیوم بررسی گردید. برای این منظور از آزمایشات با سرعت کشش ثابت استفاده شد. همچنین، به کمك مجموعه ای از اثرات کار مکانیکی و آنیلینگ نمونه ها با دانه های درشت تهیه و آزمایش شدند. دو نوع ترك ناشی از خوردگی تنشی ملاحظه گردید: ناحیه بین دانه ای ناشی از انحلال آندی تشدید شده توسط تنش و ناحیه شکست میان دانه ای به صورت کلیواژ ناشی از جذب هیدروژن.

INTRODUCTION

Fracture morphology of corrosion and stress corrosion cracking of zirconium and zircaloys in methanolic solutions has been studied by several workers [1-9]. In the case of unstressed specimens the intergranular corrosion has been observed [1-3,6-9]. Application of stress/ strain increased the proportion of intergranular separation in both zirconium and zircaloys [1-3,5,9]. A zone of transgranular cleavage has been reported [1, 3,5,9] for specimens broken under the joint action of stress/ strain and CH_3OH/HCl solutions. However, it has been emphasised that, the proportion of intergranular and transgranular was dependant upon the stress/ strain condition at the propagating crack tip as well as the test environment.

For Zircaloy-2 specimens tested in CH_3OH/HCl solutions under a plain strain condition, such as precracked double - cantilever beam specimens with an initial stress intensity close to k_{IC}, a purely transgranular cracking with no evidence of intergranular dissolution has been reported [1].

According to one report [10], the fractographic differences between split-ring specimens of Zircaloy-2 exposed to different environments, including CH_3OH/HCl solutions were mainly due to the «etching effect» of the environment on the fracture surface after the crack had passed.

Although in some reports [2], the exact details of fracture morphology and fractographic changes with the strain rate used are not clarified, it has been reported that, in dynamic testing at a high strain rate in a $CH_3OH/0.4\%$ HCl solution, the fracture mode in Zircaloy-2 (and zirconium) consisted only of ductile tearing and decreasing the strain rate induced the intergranular dissolution. It has been shown [3-5,9] that, while additions such as H_2O and arsenic (1000 ppm) to $CH_3OH/0.4\%$ HCl solution reduced the proportion of brittle fracture (i. e. intergranular, transgranular) of Zircaloy-2, the presence of platinum (25 and 1000 ppm) increased it. Also, the application of anodic potential (or currents) increased and that of cathodic potential (or current) decreased the proportion of intergranular fracture. A «dry mudd-flat» fracture feature has also been reported on the fracture surfaces of specimens tested under dynamic conditions in $CH_3OH/0.4\%$ HCl containing arsenic or platinum, as well as high anodic potentials/ currents.

In this paper, results obtained from the fractographic studies of stress corrosion crack propagation of

Zircaloy-2 in $CH_3OH/0.4\%$ HCl solution are reported. The effect of selenium, known to increase the rate of hydrogen absorption by metals in $CH_3OH/$ acid solutions [12 ,14], has also been studied.

EXPERIMENTAL PROCEDURE

Two types of single edge notch specimens were used: 120 × 20 mm for stress corrosion cracking, and 50 × 10 mm for pre-exposure tests. Specimens were prepared from 1.5 mm thick Zircaloy-2 sheet and then annealed at 800°C for 1h in a vacuum furnace. After heat treatment, all specimens were degreased with acetone and then pickled in a 5 vol% hydrofloric acid in distilled water for a total time of 120 seconds. After pickling, the specimens were washed in running water, methanol and then air dried.

Experiments were carried out using a constant crosshead speed machine. The solution used, consisted of CH_3OH and 0.4 vol% of concentrated HCl. A 25 ppm selenium (Se^{2+}) addition to CH_3OH / 0.4% HCl was also made in order to increase the rate of hydrogen absorption during the course of crack propagation. Selenium was added to CH_3OH / 0.4% HCl solution in the form of the solid selenium dioxide (SeO_2). Acid and selenium concentrations employed, were based on the results obtained from the previous works [13].

The microstructure of the as-received material consisted of fine 20-25 micron, equi-axed alpha grains. Under a combined process of deformation and annealing coarse grained material was obtained. The resultant microstructure consisted of large, approximately 150 micron, equi - axed alpha - grains.

Examination and the measurments of the maximum zone depths of the stress corrosion fracture surface features of the specimens were performed using scanning electron microscopy.

RESULTS AND DISCUSSION

1. The Effect of Crosshead Speed

The fracture surfaces of all specimens tested at crosshead speed greater than 3.3×10^{-1} $\mu m\ s^{-1}$ (0.002 (cm/min), within the range of crosshead speed used in this work, consisted of two zones: intergranular region at the specimen edges and notch root, with ductile tearing in the remainder of the specimen (Figure 1). However, as the crosshead speed decreased, the intergranular zone depth increased and, as a result, the amount of ductile tearing decreased.

At a crosshead speed of 8.3×10^{-1} $\mu m\ s^{-1}$ (0.005 cm/min) a discontinuous zone consisting of grooves and channels, or highly striated area, appeared on the fracture surface between the intergranular and ductile component of fracture in the centre. This type of fracture surface has also been reported[15]for titanium alloys and is termed as 'Flutings'.These fluted areas were found to occur more frequently and had penetrated further into the specimens tested at a crosshead speed of 6.6×10^{-1} $\mu m\ s^{-1}$ (0.004 cm/min),

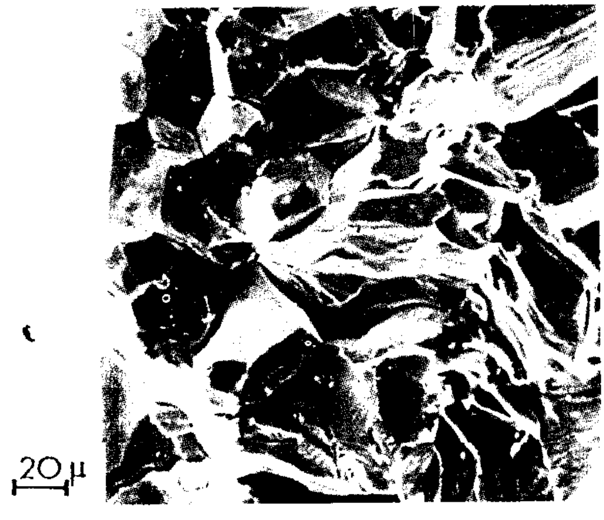

Figure 1. An intergranular/ ductile tearing fracture: 8.3×10^{-1} $\mu m\ s^{-1}$

Figure 2. An area consisting of grooves and channels or striation, named «Flutings»: 6.6×10^{-1} $\mu m\ s^{-1}$

(Figure 2). The flutings appeared to be perpendicular to the general crack propagation direction at an angle of approximately 90 degrees to the specimen edges.

The fracture surface of the specimens tested at a crosshead speed of 3.3×10^{-1} μm s^{-1} (0.002 cm/min) revealed a distinct three zone fracture morphology (Figure 3), consisting of an intergranular zone at the notch root and edges followed by a transgranular cleavage zone and finally a region of ductile tearing. However, at this crosshead speed, some dispersed areas of fluting were occasionally observed. The three zone fracture surface was present in all the specimens tested at crosshead speeds beetween 3.3×10^{-1} - 6.6×10^{-3} μm s^{-1} (0.002 - 0.00004 cm/min).

As the crosshead speed decreased, the amount of intergranular and transgranular fracture increased and that of ductile tearing diminished. The intermediate transgranular cleavage zone was more discontinuous at the upper end of the crosshead speed range where three zone fracture prevailed, but became more continuous and pronounced as the crosshead speed decreased.

The general direction of the transgranular cleavage propagation appeared to be perpendicular to the general direction of crack propagation. However, some transgranular facets were observed which were propagated in the direction of general crack propagation. The phenomenon could be attributed to either the random orientation of the grains through which the crack passed, or the crack may have initiated on the exposed flat surface of the specimen, due to stress concentration and corrosive attack, and propagated across the width of the specimen.

Specimens fractured at the lower range of crosshead speed used, i. e. equal or less than 6.6×10^{-3} μm s^{-1} (0.00004 cm/min) revealed only a two zone fracture morphology consisting of an intergranular zone at the edges and notch root followed by transgranular cleavage in the rest of the specimen. The ductile tearing zone was apparently absent except at the mechanically broken end of the specimens. Also, as the crosshead speed decreased the size of transgranular cleavage zone increased at the expense of the intergranular zone.

2. The Effect of Selenium Addition

The previous results[13] obtained from the investigation carried out in $CH_3OH/0.4$ HCl solution plus various selenium content (25-1000 ppm) showed that, the maximum susceptibility to stress corrosion cracking was obtained at a concentration of 25 ppm selenium addition. For a given crosshead speed, observation revealed a greater ratio of brittle fracture to ductile tearing for specimens fractured in $CH_3OH/0.4\%$ HCl solution with 25 ppm selenium addition than without. The observed relationship between the fracture surface features and the crosshead speed, could be summarized as follows.

At a crosshead speed greater than 3.3 μm s^{-1} (0.02 cm/min) a two zone fracture surface, i. e. an outer intergranular and a central ductile tearing, was observed. For a given crosshead speed, no appreciable effect on the intergranular zone depth was observed due to the selenium addition. Traces of transgranular cleavage were observed occasionally on the fracture surface of specimens fractured at crosshead speed of

Figure 3. A three zone, intergranular/cleavage/ductile tearing: 3.3×10^{-1} μm s^{-1}

Figure 4. «River patterns» transgranular cleavage: 6.6×10^{-3} μm s^{-1}

$3.3\ \mu m\ s^{-1}$ (0.02 cm/min)

At a crosshead speed within the range of $1.6 - 1.3 \times 10^{-2}\ \mu m\ s^{-1}$ a typical three zone stress - corrosion crack propagation, i. e. intergranular/ cleavage/ ductile tearing, was observed. In general, at a given crosshead speed. addition of 25 ppm selenium increased the fraction of brittle fracture. At the very low end of crosshead speed range employed (but still beyond $1.3 \times 10^{-2}\ \mu m\ s^{-1}$), and for a given crosshead speed, addition of 25 ppm selenium decreased the intergranular zone depth. This was accompanied by an increase in the amount of cleavage fracture.

Only two zone fracture surface features, i. e. intergranular and transgranular cleavage, were observed on the fracture surface of the specimens fractured at a crosshead speed less than $1.3 \times 10^{2} \mu ms^{-1}$. For a given crosshead speed, the amount of intergranular apeared to be less and the fraction of transgranular cleavage more in specimens fractured in $CH_3OH/0.4\%$ HCl solution with selenium addition than without it. This could be attributed to the flux of hydrogen absorbed by deformed zone at a slowly propagating intergranular crack tip. Increasing the amount of hydrogen absorbed by selenium addition increased the amount of cleavage observed and raised the maximum crosshead speed at which cleavage is observed.

3. Grain Size Dependence

In order to study the fracture surface features, especially transgranular cleavage, more extensively, specimens with large grain size structure were tested under the same conditions as the previous ones. The range of crosshead speed selected ($3.3 \times 10^{-1} - 6.6 \times 10^{-3} \mu ms^{-1}$) for these experiments was for general comparison with the results obtained for fine grained materials

Figure 5. «Fan shaped» cleavage facets: $6.6 \times 10^{-3}\ \mu m\ s$

In general the fracture surfaces of all grained specimens fractured in $CH_3OH/0.4\%$ HCl with and without selenium addition were similar to that observed for fine grained material. However, the transgranular cleavage observed on coarse grained specimens was more pronounced than on the fine grained ones. An area of a fracture surface consisting of transgranular cleavage characterized by "river patterns" is shown in Figure 4. A part from river patterns, another special type of transgranular cleavage fracture surface feature was observed, which was named «Fan shaped cleavage facets» (Figure 5). Next to the transgranular cleavage regions, areas showing the highly parallel striations (i. e. fluting) were sometimes evident (Figure

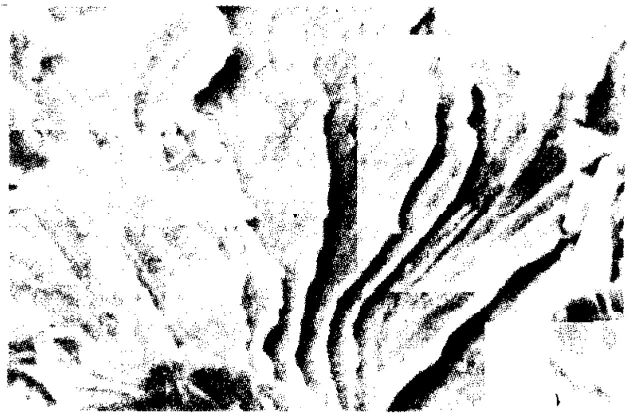

Figure 6. The relationship between river pattern cleavage and fluting on one grain: $6.6 \times 10^{-3}\ \mu m\ s^{-1}$

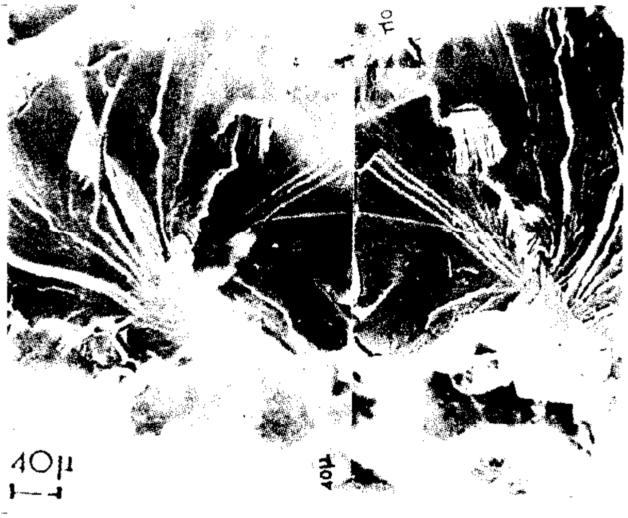

Figure 7. Fractograph of one area on both faces of the fracture surface. The complementary (interlocking) characteristic of cleavage is clearly visible: $1.6 \times 10^{-2}\ \mu m\ s^{-1}$

6). This type of fracture often produces features consisting of nearly hexagonal blocks, which suggests that the striations were produced on planes almost at right angles to the basal cleavage planes.

Examination of both faces of fractured specimens containing both cleavage and striations (fluting) revealed more information about the origin and nature of these types of fracture surface features. The cleavage areas were always complementary, i. e. interlocking surfaces. This is apparent in Figure 7, where corresponding areas appear raised on one surface but depressed on the other surface. However, unlike cleavage features, the flutings are not complementary. In this case, corresponding features of the striations are raised or depressed on both surfaces, so that the striations have a mirror image print of one surface with the other.

4. Maximum Zone Depth of the Fracture Surface Features

In order to elucidate the nature and mechanism of intergranular and transgranular cleavage features observed during the course of this work, the maximum zone depth of intergranular corrosion was compared with the maximum zone depth of intergranular stress corrosion (Figures 8, 9). This comparison was made for identical periods of exposure. Also, the maximum zone depths of intergranular, transgranular cleavage and ductile tearing on the fracture surfaces of stress corrosion cracked specimens in both solutions, i. e. with and without selenium additions, were measured and compared (Figures 10, 11).

Figures 8 and 9 show that, for both solutions, over a wide range of crosshead speeds the intergranular separation of stress corroded specimens is more than corroded ones. This can easily be explained as arising from stress/strain assisted dissolution. At very high crosshead speeds, i. e. more than 1 $\mu m\ s^{-1}$, the difference might be expected to disappear. This is because such experiments occupy a very short period of time.

For the crosshead speeds lower than $10^{-2}\ \mu m\ s^{-1}$ the difference between the two types of intergranular is reduced again. It can be seen that it is replaced by transgranular cleavage (Figures 10, 11). The disappearance of stress assisted intergranular fracture and replacing it by transgranular cleavage could be explained by the effect of the applied crosshead speed upon the imposed stress.As the applied cross head speed is lowered the time taken to initiate the intergranular stress corrosion will increase.Duging all this time hydrogen is being absorbed. In the low crosshed speed experiments, the amount absorbed is great enough to cause transgranular cleavage before the stress is sufficiently high to cause intergranular stress corrosion.

At the very low end of crosshead speeds used, for $CH_3OH/0.4\%$ HCl solution, the maximum intergranular corrosion depth is more than the maximum intergranular stress corrosion depth (140 and 110 μm, respectively) while for $CH_3OH/0.4\%$ HCl solution with selenium addition, the reverse is observed (70 μm and 90 μm, respectively). This is due to the more corrosiveness effect of $CH_3OH/0.4\%$ HCl solution compared with $CH_3OH/0.4\%$ HCl solution plus 25 ppm selenium additions, as well as the more hydrogen absorption in the latter environment.

Comparison ofFigures 10 and 11 show that, at a given crosshead speed, the amount of transgranular cleavage observed on the fracture surface of the specimens broken in $CH_3OH/0.4\%$ HCl solution with 25 ppm selenium addition is always more than that observed in $CH_3OH/0.4\%$ HCl solution without it. The observed effect due to the addition of selenium cathodic poison upon the fracture surface features is consistent with the previously proposed function of absorbed hydrogen atoms, produced by cathodic reaction (i. e. $H^+ + e \rightarrow H_{atm}$).

CONCLUSIONS

From the results obtained in this study, the following conclusions can be drawn:

1. Decreasing the crosshead speed increases the brittle fracture (i. e. intergranular dissolution and transgranular cleavage) and decreases the ductile tearing.
2. The addition of 25 ppm selenium to methanol/0.4% HCl solution, increased the occurrence of transgranular cleavage. This could be associated with an increase in the possibility of the formation of a high hydrogen concentration region ahead of the progagating crack.
3. Both types of transgranular cleavage observed, i.e. «River patterns» and «Fan shaped», were always complementary, i. e. interlocking surfaces on both parts of specimens.
4. Flutings observed during this work were due to ductile tearing and often produce features consisting of nearly hexagonal blocks which suggestthat the striations were produced on

planes almost at right angles to the basal cleavage planes.

5. Intergranular stress corrosion cracks of Zircaloy-2 in CH_3OH/HCl solutions is caused by stress assisted anodic dissolution and hydrogen plays no part in it.
6. Transgranular cleavage observed in Zircaloy-2 during this work is believed to have occurred due to a process of hydrogen absorption.

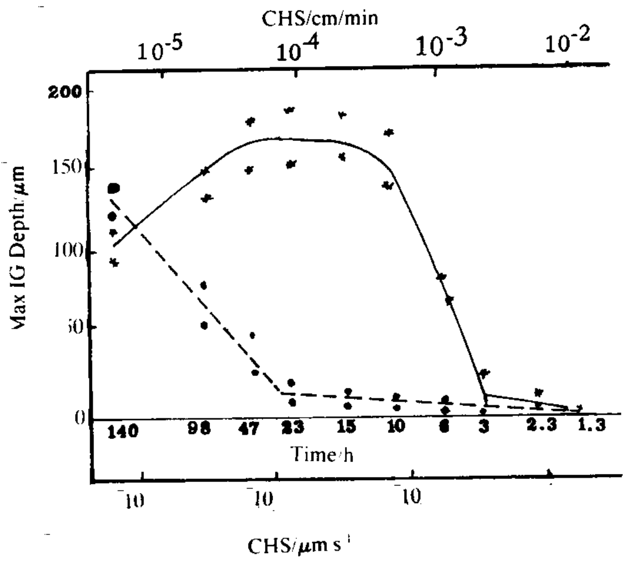

Figure 8. The maximum intergranular zone depth in correoded (● —— ●) and stress corroded (★ —— ★) specimens:) $CH_3OH/0.4\%$ HCl

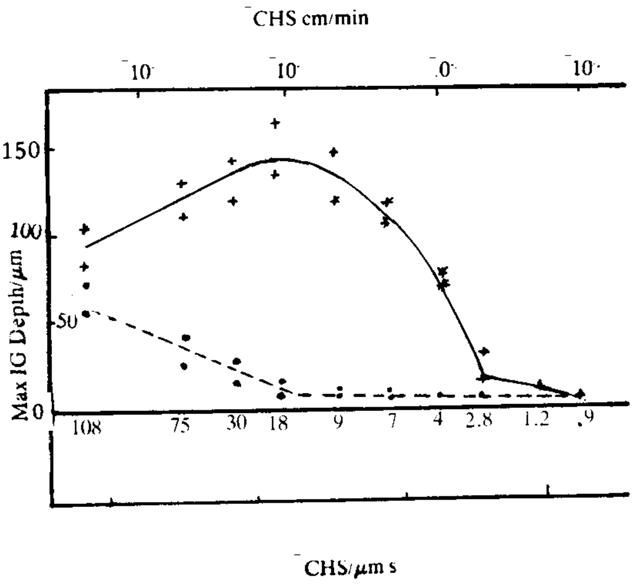

Figure 9: The maxium intergranular zone depth in corroded (●-●) and stress corroded (★—★) specimens: $CH_3OH/0.4\%$ HCl/25ppm selenium

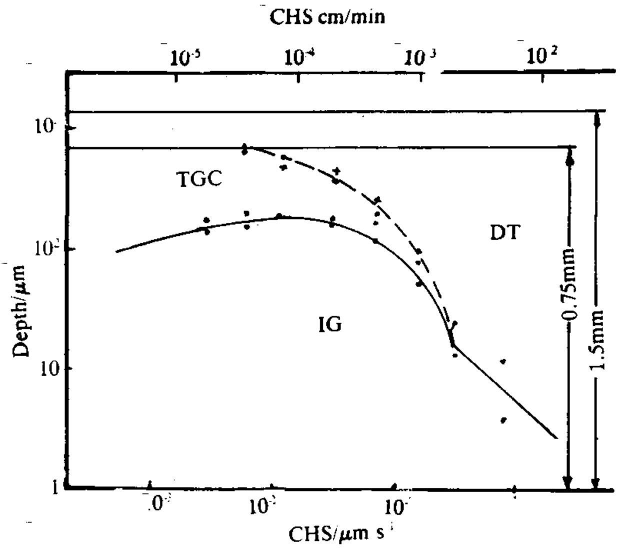

Figure 10: The maximum zone depths of intergranular, cleavage and ductile tearing: $CH_3OH/0.4\%$ HCl

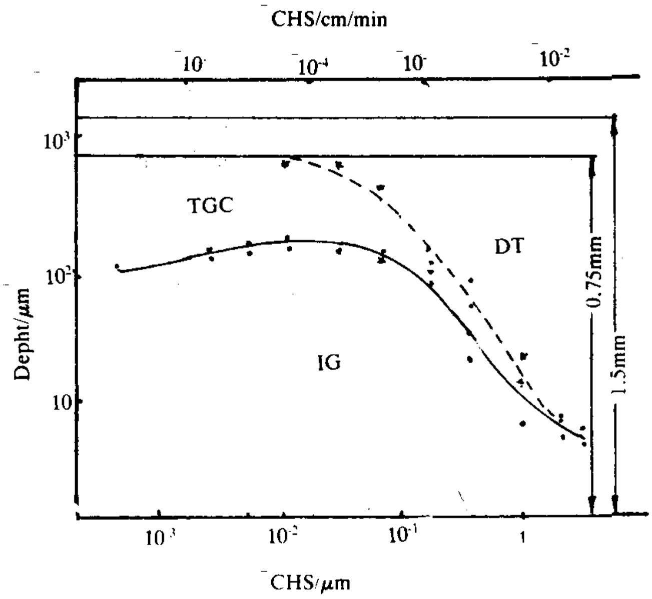

Figure 11. The maximum zone depths of intergranular, cleavage and ductile tearing: $CH_3OH/0.4\%$ HCl/25 ppm

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