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Hydrogen, Hydrides, and Crack Tip Deformation in Titanium

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ABSTRACT

This paper summarizes results obtained in our laboratory on the susceptibility of commercial purity titanium and the α/β titanium alloy Ti-5111 to hydrogen cracking. The tests were run under cathodic polarization in sodium chloride solutions. Cathodic potentials as low as $-1400\text{mV}_{\text{SCE}}$ had little effect on the mechanical properties of grade 2 titanium, but grade 3 titanium showed a decrease in the elongation to failure as the electrochemical potential became more cathodic. However, the fracture mode remained ductile with microvoids nucleating at hydrides. Ti-5111 was very susceptible to hydrogen cracking when the pH of the solution was low and the electrochemical potential was cathodic, but hydrides did not appear to play a role in the cracking process.

KEYWORDS

titanium, hydrogen embrittlement, sodium chloride solutions, Ti-5111

INTRODUCTION

The mechanisms of hydrogen embrittlement have been a topic of great debate in past years. One reason for this is that the actual mechanism can vary significantly from one materials system to another [1]. In some materials, such as titanium and zirconium, the primary cause of embrittlement appears to occur through hydride formation. In other materials, such as steel and nickel-base materials, atomic hydrogen appears to be the primary cause of embrittlement. More recent studies of intermetallic compounds have suggested that the source of hydrogen is very important [2]. For example, in FeAl the presence of atomic hydrogen in the environment does not appear to have a great effect on mechanical properties, whereas water vapor can cause a significant decrease in elongation to failure.

Although one single mechanism will not explain hydrogen embrittlement, it is important to have complete descriptions of this problem in all important structural materials. We have recently examined hydrogen embrittlement in various grades of commercial purity titanium as well as in titanium alloys. The results show that in commercial purity titanium hydrides play a dominant role in causing embrittlement, whereas in the α/β alloys they may play no role at all. By comparing these materials one can understand the different mechanisms that lead to embrittlement.

EXPERIMENTAL

In this paper we will discuss three different materials. Two of the materials were commercial purity titanium and the third was an α/β alloy, Ti5111. Their compositions are listed in Table I along with their basic mechanical properties. All were tested in the as-received condition. The two commercial purity titanium materials had an equiaxed grain structure and the Ti-5111 had a lamellar α/β microstructure.

The mechanical tests for these materials were all performed on single-edge notched sheet tensile samples. The thickness of the grade 2 and grade 3 samples was 1.12 mm and 0.62 mm, respectively, and that of the Ti-5111 was 2.56 mm. The notch had an included angle of 60°. The samples were pulled to failure in a 3.5% solution of sodium chloride under various applied electrochemical potentials. We used the ratio of the elongation to failure in the sodium chloride solution to that in an inert oil held at the same temperature as a measure of susceptibility to hydrogen embrittlement. We will refer to this parameter as the elongation ratio in the text below. All tests were run with the solution at 70°C. The pH of the solution used to test the commercial purity titanium was 1 and that used for the Ti-5111 was either 1 or 8. More details of the testing and post-test examination have been given in references 3 -5.

Table I
Alloy Composition and Mechanical Properties

Alloy	Composition (wt.%)	Yield Strength (MPa)	UTS (MPa)	Elongation to Failure
Grade 2	Ti-0.14O-0.02C-0.008N-0.08Fe	344	506	28
Grade 3	Ti-0.21O-0.01C-0.009N-0.16Fe	489	603	24
Ti-5111	Ti-5Al-1Sn-1Zr-1V-0.08Mo	750 (nominal)	Not Measured	Not Measured

RESULTS

Figure 1a shows the elongation ratio for grades 2 and 3 titanium plotted as a function of electrochemical potential. The results show that there is very little change in the elongation ratio for grade 2 titanium as the electrochemical potential is made more cathodic. This result was obtained, even though other experiments had shown that hydrides begin to form in this material at electrochemical potentials below –600 mV_{SCE} and that thick layers of hydrides are formed at potentials near –1400 mV_{SCE}. In contrast, grade 3 titanium showed a measurable loss in the elongation ratio as the electrochemical potential was made more cathodic. Figure 1b shows the elongation ratio at –1400 mV_{SCE}

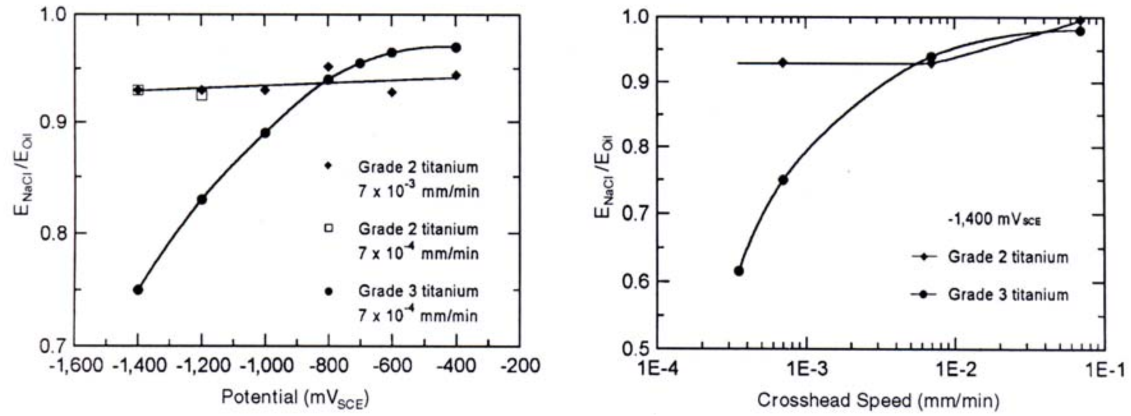

Figure 1: (a.) The elongation ratio plotted as a function of electrochemical potential for grade 2 and grade 3 titanium. The crosshead speeds are given in the figure. (b.) The elongation ratio plotted as a function of crosshead speed for grade 2 and grade 3 titanium.

for both grade 2 and grade 3 titanium plotted as a function of crosshead speed. The results show that as the crosshead speed decreased the elongation ratio stayed approximately constant for grade 2 titanium, whereas the elongation ratio dropped for samples of the grade 3 titanium.

Examination of the fracture surfaces showed that under all conditions the grade 2 titanium underwent ductile failure. An example is shown in Figure 2a. The grade 3 titanium had a similar fracture surface when tested in oil or under anodic conditions. However, as the elongation ratio decreased for the grade 3 titanium, the fracture surface showed new features. These included brittle secondary cracks on the surface, some evidence of large voids on the surface, and evidence of a new population of fine scale voids. A micrograph is shown in Figure 2b. Additional information was obtained by examining the hydride that formed on the surface of a sample after cathodic charging. In the case of the grade 2 titanium, we found that there was a thick layer of hydrides, as shown in Figure 3a, but that beneath this layer few hydrides were observed. In the grade 3 material, this thick layer was also observed, but in addition there were hydrides beneath this thick layer extending into the matrix, as shown in Figure 3b. In flat samples charged for 24 hours at an electrochemical potential of –1000 mVSCE, hydrides extended

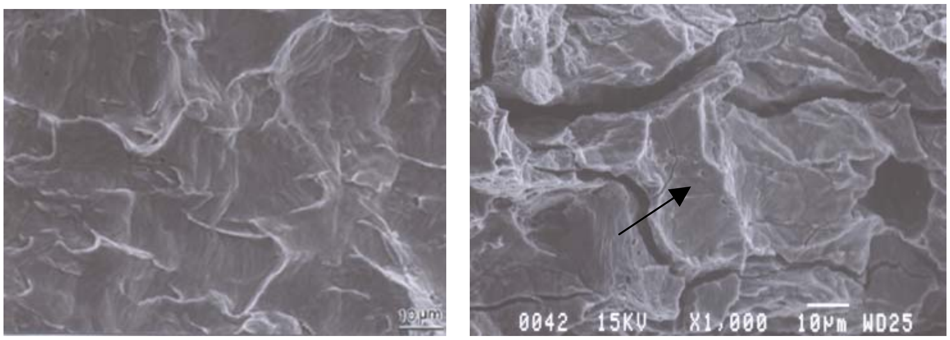

Figure 2: Scanning electron micrographs of (a.) grade 2 titanium tested at –400 mV_{SCE} and (b.) grade 3 titanium tested at –1400 mV_{SCE}. The arrow points out fine microvoids.

approximately 50 µm into the bulk and for an electrochemical potential of –1400 mV_{SCE} the hydrides extended approximately 90 µm into the bulk.

We also examined samples in which the crack had been stopped before proceeding completely through the sample. In the grade 2 material we always found a blunted crack, as shown in Figure 4a, with no evidence of cracking ahead of the rounded crack tip. In contrast, in the grade 3 material we found a sharper crack extending from the blunted crack tip, with evidence that microvoids were forming ahead of this blunted crack and that these microvoids were connecting up to allow the crack to extend.

We now consider the results for Ti-5111. Figure 5 shows the elongation ratio of this material plotted as function of applied potential. In the pH=8 solution, there was no loss in elongation even though the electrochemical potential was very cathodic. In contrast, in the pH=1 solution the elongation ratio was essentially zero when the electrochemical potential was below –1000 mV_{SCE}. The fracture surfaces of the samples that showed no elongation to failure were very brittle, and examination of propagating cracks in these samples showed that they tended to go through the β-phase (5). There was no evidence of hydride formation in these samples, even though in the pH=1 solution the hydrides were found to precipitate at potentials below –500 mV_{SCE}. However, these

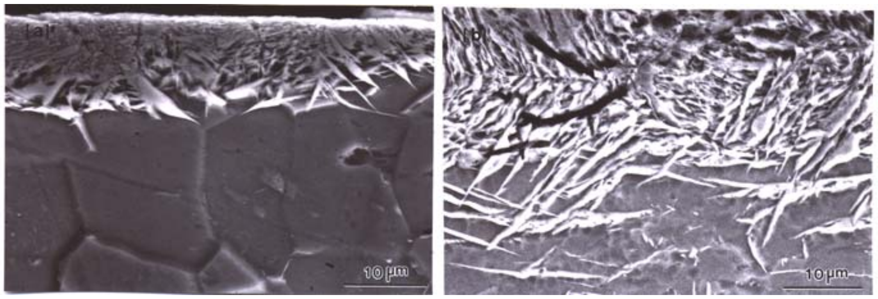

Figure 3 : Scanning electron micrographs of hydrides on the surface of (a.) grade 2 and (b.) grade 3 titanium after cathodic charging.

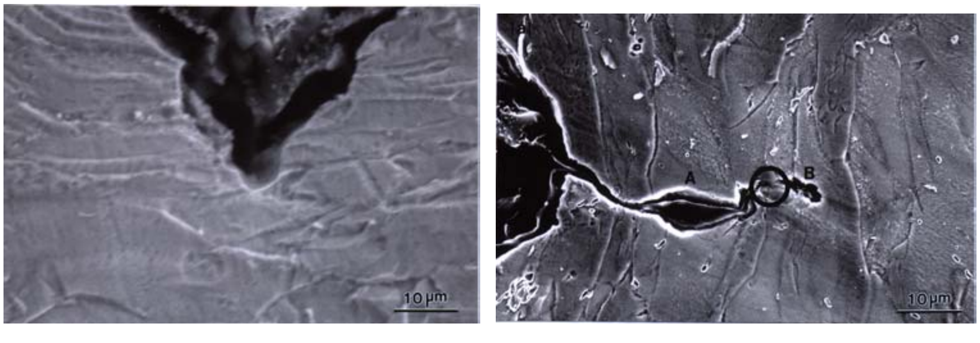

Figure 4 : Scanning electron micrograph of a crack tip in (a.) grade 2 titanium and (b.) grade 3 titanium. Both tests were performed at –1400 mV_{SCE}. The circle in Figure 4b highlights a region where the crack is connecting up between two microvoids.

samples failed so rapidly that there was insufficient times for the hydrides to nucleate and grow to any extent.

DISCUSSION

In general, hydrogen cracking is thought of as a brittle fracture mode. In steels, nickel-base alloys, and intermetallic compounds where atomic hydrogen is the embrittling species, the fracture mode is usually transgranular cleavage or intergranular fracture. Both of these fracture modes are associated with very limited ductility. In systems where hydrides form, the fracture mode is also usually reported to be brittle [1]. The most general models suggest that hydrides form at the crack tip in the tensile field of the crack. These hydrides then fracture in a brittle manner or a crack forms along the hydride-matrix interface.

In our study of the grade 2 and grade 3 titanium, we found no evidence of brittle failure. The fracture mode remained ductile, even though a decrease in the elongation ratio was found for the grade 3 material. Our results suggest that hydrides nucleate in the matrix in front of the crack tip. These hydrides then act as sights for microvoid formation. As the stress in front of the crack tip increases, these microvoids connect up, leading to crack advance. New hydrides then form in front of the crack tip and the process is repeated. In the grade 2 material, the hydrides do not form in front of the crack tip and this process does not occur. The reasons why the grade 3 material forms hydrides in front of the crack tip whereas the grade 2 material does not form these hydrides has been discussed in previous publications [4,6]. In short, we propose that the main reason for this difference is the lower solubility of hydrogen in grade 3 material as a result of its higher interstitial content. In addition, the higher yield strength of the grade 3 material may contribute to its greater susceptibility to hydride-induced ductile failure.

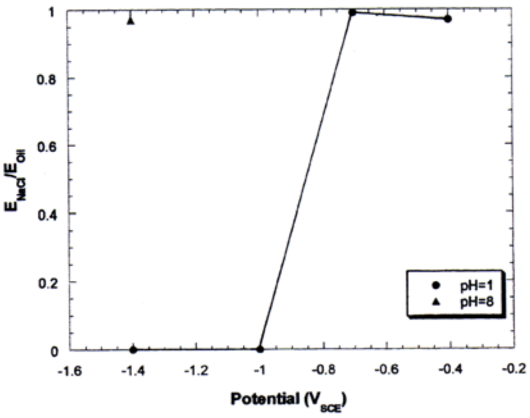

Figure 5: The elongation ratio plotted as a function of the electrochemical potential for Ti-5111. Results are shown for tests run in both pH=1 and pH=8 3.5%NaCl.

When β-phase is present in the material but does not provide a continuous path through the material, the fracture mode should be similar to that reported above. This idea is consistent with the results of Nelson and Williams on Ti-6Al-4V [7,8]. Once the β-phase forms a continuous pathway, as it does for Ti-5111, the mechanism of hydrogen embrittlement changes significantly. The β-phase has a higher solubility of hydrogen than does the α-phase, and hydrogen will diffuse more rapidly into the β-phase. Thus when the sample is tested in a sodium chloride solution under conditions where hydrogen is generated, the atomic hydrogen will quickly diffuse into the material through this phase and be primarily concentrated there. This high concentration then leads to embrittlement. This result is again similar to that reported by Nelson and Williams for Ti-6Al-4V that had been heat treated to have a continuous β-phase [7,8]. They found cracking along the α/β interfaces and that the fracture mode was a brittle cleavage along the α/β interface.

CONCLUSIONS

This paper has presented results for hydrogen embrittlement in three titanium-base materials. Two were commercial purity titanium in which only the α-phase was present. The third was an α/β alloy. The results showed in the commercial purity titanium that the embrittlement occurred through the formation of hydrides. However, the fracture was completely ductile and the hydrides acted as sights for void nucleation and growth. These voids were then connected up through a fracture process that led to crack advance. Thus, precipitation of hydrides in front of the crack tip is a critical feature of this model. In the α/β material, the fracture was brittle. As shown in reference 5, the crack propagated through the β-phase, which has a higher solubility for hydrogen and also provides a faster diffusion path. Thus by a change in the microstructure of the material, the fracture mode changes significantly.

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