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THE MECHANISM OF STRESS-CORROSION CRACKING OF Ti-6Al-4V ALLOY IN ANHYDROUS METHANOL

H. L. GEGEL
S. FUJISHIRO

TECHNICAL REPORT No. AFML-TR-68-290

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The distribution of this report is limited because the information is restricted to prevent premature release of data on synthesized potential high-strength alloys of interest to National Defense.

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FOREWORD

This report was prepared by the Advanced Metallurgical Studies Branch, Metals and Ceramics Division, Air Force Materials Laboratory. The principal investigators for this project were H. L. Gegel and S. Fujishiro. This program was initiated under Project No. 7353, "Characterization of Solid Phase and Interphase Phenomena in Crystalline Substances," Task No. 735302, "Correlation of Physical and Mechanical Properties of Metals and Ceramics," during the period January 1968 through June 1968. Funds for this project were supplied to the Air Force Materials Laboratory by the Office of Aerospace Research. The work was administered by the Advanced Metallurgical Studies Branch under the direction of Dr. H. L. Gegel.

Mr. Larry Bates of the Systems Research Laboratory, Contract F33615-67-C-1421, is greatfully acknowledged for his assistance in electron microscopy. Mr. C. Michael Swinning of The Ohio State University, Department of Metallurgical Engineering, contract AF33(615)-5108, is also acknowledged for his support in the studies on stress-corrosion cracking.

This report was submitted by the authors in June 1968 for publication.

This technical report has been reviewed and is approved.

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ABSTRACT

Electron fractographic and high resolution electron diffraction studies of the fracture surface of Ti-6Al-4V alloy specimens were tensile tested at 1.7 x 10^{-5} sec^{-1} in anhydrous methanol. The tests revealed a hard second phase on the fracture surface and showed it to be TiH_2 associated with the presence of Ti_3Al. The crystallographic relationships of α , β , Ti_3Al, and TiH_2 were determined from the electron diffraction pattern, and were in agreement with the expected relationships reported in the literature. The results support the conclusions made by Scully that stress-corrosion cracking in high aluminum containing titanium alloys is a form of hydrogen embrittlement.

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SECTION I

INTRODUCTION

The mechanism of stress-corrosion cracking of titanium alloys in methanol and acidified methanol has been of recent interest. Titanium alloys containing aluminum have exhibited brittle behavior in these environments, and Sanderson, Powell, and Scully (Reference 1) described the embrittling mechanism as a form of hydrogen embrittlement. Sanderson and Scully (Reference 2) also observed that the hydride forms in a susceptible alloy when deformed in an environment which causes cracking, do not form in an environment which does not cause stress-corrosion cracking. Margolin and Pertisch (Reference 3) have shown that hydrogen absorption on etching will increase with increasing amounts of Ti_3Al. Since investigations by Sagel, Schulz, and Zwicker (Reference 4) and Crossley (Reference 5) have established the existence of various ordered phases based on alpha titanium at contents greater than 5.5% aluminum, it is possible for the Ti-6Al-4V alloy to become susceptible to stress-corrosion cracking by a form of hydrogen embrittlement described by Sanderson and Scully.

In this report, fractographic and high resolution electron diffraction evidence and the results of mechanical testing are shown to support the mechanisms proposed by Scully.

SECTION II

EXPERIMENTAL METHODS

The investigations were confined to Ti-6Al-4V sheet alloy supplied by the Titanium Metals Corporation of America (TMCA). The dimensions of the sheet were 0.0048 inch thick and 3 ft wide x 50 ft long. The composition of the major elements in the alloy is 6.75% Al, 4.0% V, 0.30% Fe, 0.20% oxygen, 0.10% carbon, 0.05% nitrogen, and 0.015% hydrogen. A two-stage plastic-carbon replicating technique was used to examine the microstructure before and after fracturing in anhydrous methanol. Kroll's etchant was used to reveal the general microstructure of the alloy. The composition of this etchant is 2 parts HF, 6 parts HNO_3, and 92 parts distilled water. A replica of the as-received microstructure is presented in Figure 1.

All tensile specimens were tested in spectroquality reagent methanol having an ultraviolet cut-off of 205 $m\mu$, 0.05% water, 0.0003% evaporation residue, and a maximum fluorescence of 0.25 ppb as quinine base. Subsize tensile specimens cut parallel to the rolling direction were used in this study. The specimens had a 1/2-inch gage length, a 0.1-inch width in the gage section, and a 1/32-inch radius at the shoulder. A Teflon cell was used to contain the environment, and the grips and pull rods exposed to the environment were coated with a stop-off lacquer called "Miccrostop". A table model Instron Testing Instrument Model TM-M-L (Metric-Slow Speed) was used to obtain the load-elongation data, and all specimens were tested at a single strain rate of 1.7×10^{-5} sec^{-1}.

High resolution electron diffraction on the fracture surface was performed on a JEM-6A electron microscope to identify the hard particles shown in Figure 2. The section of the surface was mounted parallel to the incident beam below the intermediate lens in order to improve the resolution of the electron diffraction pattern. The camera length at this position is not influenced by a change of lens current.

SECTION III

EXPERIMENTAL RESULTS

1. MECHANICAL PROPERTIES

The average mechanical properties of the starting material tested in air are 76 kg/mm^2 yield strength, 126 kg/mm^2 ultimate strength, and 7% elongation. The average values for specimens in methanol are 76.0 kg/mm^2 yield strength, 128.0 kg/mm^2 ultimate strength, and 6.5% elongation. Typical stress-strain curves for specimens mechanically tested in air and methanol are presented in Figure 3. The stress-strain curve for the specimen tensile tested in methanol has a larger work hardening coefficient than the tensile specimens deformed in air. This behavior is characteristic of specimens having a dispersed second phase that is widely separated (Reference 6). The average elongation is only 1/2-inch less than that for air tested specimens, but it is a change that is commensurate with an increase in the work hardening coefficient caused by a second phase of low volume fraction.

Some of the as-received material was given an anneal at 500° and 600°C for 48 hours to determine whether heat treatment would promote an ordering reaction. The data for this heat treatment is presented in Table I. A considerable increase in the yield strength and percent elongation in both air and methanol was achieved by this annealing treatment. The spread, $\Delta\sigma$, in strength difference between the ultimate strength and the yield strength was decreased making the slope $(\partial\sigma/\partial\epsilon)_\epsilon$ at any value of strain, ϵ, less than that for the as-received condition. Since grain growth did not occur after annealing, the decrease in $(\partial\sigma/\partial\epsilon)_\epsilon$ is considered to be related to the ordering of aluminum atoms. The effect of ordering on the shape of the stress-strain curve has been discussed by Haasen (Reference 7), and a comparison of the shapes of the respective stress-strain curves is shown in Figure 3. Although annealing at 500° and 600° C increases the amount of elongation from 7% to approximately 11% in air, testing in methanol still reduces the amount of total elongation with respect to air.

TABLE I

COMPARISON OF MECHANICAL PROPERTIES IN DIFFERENT ENVIRONMENTS AND FOR HEAT-TREATMENTS.

	Air			Methanol		
	Y.S (kg/mm^2)	U.T.S. (kg/mm^2)	Elong. (%)	Y.S. (kg/mm^2)	U.T.S. (kg/mm^2)	Elong. (%)
As-received	176	126	7.0	176	128	6.5
500° C, 48 hrs.	150	113	10.5	103	112	8.9
600° C, 48 hrs.	102	112	11.2	103	115	10.6

2. ELECTRON FRACTOGRAPHS

Electron fractographs taken of tensile specimens fractured in air and anhydrous methanol are presented in Figures 2 and 4. The difference in the two fractographs lies mainly in the presence of a hard second phase on the fracture surface of the specimen ruptured in the methanol environment. Both fractographs are characteristic of failure by a shear rupture mode. It is generally believed that the parabolic dimples result from the coalescence of voids which form at places where nondeforming, hard particles have separated from the matrix along the particle-matrix interface. Since only the specimens fractured in anhydrous methanol show the parabolic dimples nucleating from hard particles, the environment appears to have been responsible for their formation.

3. HIGH RESOLUTION ELECTRON DIFFRACTION

In order to identify the hard particles observed on the fracture surfaces of specimens tensile tested in anhydrous methanol, high resolution electron diffraction analysis was performed on the surface. Figure 5 represents a typical electron diffraction pattern. The pattern was most pertinently interpreted in terms of and β titanium, Ti_3Al, and TiH_2. Two crystallographic structures were reported for the hydride. One structure was face-centered cubic with $a_0 = 4.40$ Å (Reference 8) and the other was body-centered tetragonal having $a_0 = 3.12$ Å and $c_0 = 4.18$ Å (Reference 9). The body-centered tetragonal hydride is reported to be the stable form below 260°C.

The present result was indexed best in terms of body-centered tetragonal with 5% accuracy in both lattice parameters and the angular relationship of the planes. The diffraction spots from the hydride phase consists of two or more smeared weak points. This fact may indicate a small misorientation of the hydride with respect to the matrix and variation in the lattice parameters due to a non-equilibrium condition. Evidence for the formation of the hydride under the experimental conditions is also supported by the morphology of the precipitates which were observed in the vicinity of the fracture. There are some conflicts in the exact value for the solubility limit of aluminum in titanium (Reference 10). According to the studies by Sagel et al (Reference 4) and Crossley (Reference 5), the solubility limit of aluminum in the titanium rich end is as low as five weight percent at 500° C. The material under investigation was stress relief annealed in this temperature range before further reduction in area by rolling it to 0.0048 inch thickness, so it is probable that Ti_3Al could have formed during these annealing processes.

The orientation relationships of the phases thus determined are as follows:

$$\begin{array}{llll}
\{0001\}_\alpha \parallel \{11\bar{2}0\}\ Ti_3Al & & \{0001\}_\alpha \parallel \{\bar{1}10\}_\beta \\
<10\bar{1}0>_\alpha \parallel <0001>\ Ti_3Al & & <10\bar{1}0>_\alpha \parallel <001>_\beta \\
\{11\bar{2}2\}_\alpha \parallel \{110\}_H & & \\
<10\bar{1}0>_\alpha \parallel <1\bar{1}0>_H & &
\end{array}$$

Margolin and Pertisch (Reference 3) observed recently that the solubility of hydrogen in titanium was enhanced by increasing Ti_3Al contents. Since the Ti-6Al-4V alloy investigated had 6.75 weight percent aluminum, it is conceivable that hydrogen absorption plus plastic deformation facilitates the nucleation of titanium hydride along the interfaces of the coexisting phases.

SECTION IV

DISCUSSION

The mechanism of stress-corrosion cracking of Ti-6Al-4V in anhydrous methanol appears to result from a form of hydrogen embrittlement when the alloy is in a susceptible condition and in a methanol environment capable of causing cracking. Recent studies by Sanderson and Scully (Reference 2) and particularly Margolin (Reference 3) support the idea that an alloy becomes susceptible when the aluminum content is > five weight percent which is the aluminum content where various ordered phases begin to appear in the microstructure (References 4, 5, 11). Cracking in Ti-6Al-4V occurs as the result of hydrogen ingress along the interfaces of the alloy which eventually results in titanium hydride formation during deformation. Hydride formation leads to a region of highly localized work hardening which promotes crack initiation. Since the deformation process in titanium alloys is limited to slip on $\{10\bar{1}0\}$ planes, along $<11\bar{2}0>$ directions, the propagation of crack growth is enhanced by dislocation configurations that restrict the growth of the plastic constraint region which blunts propagating cracks. Ti_3Al particles or regions of short-range order reported for Ti-6Al-4V by Williams and Blackburn (Reference 11) plus the presence of the environmentally induced hydride increases the local stress concentration associated with dislocation pile-ups by confining them to their slip plane $\{10\bar{1}0\}_\alpha$. The fractographic and high resolution electron diffraction evidence supports the idea that stress-corrosion cracking in anhydrous methanol is a form of hydrogen embrittlement that occurs when aluminum-containing alloys are made susceptible to hydrogen embrittlement by the presence of Ti_3Al or ordered regions in the microstructure.

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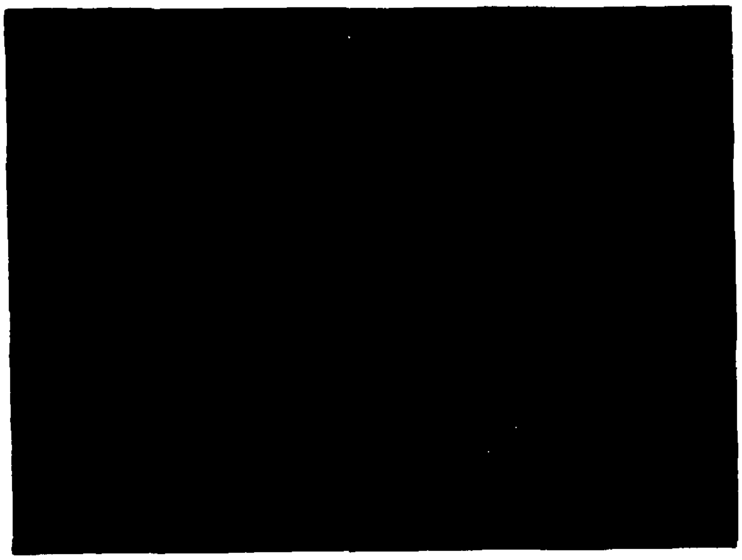

Figure 1. Electron Micrograph of As-Received Ti-6Al-4V Microstructure 1700X

Figure 2. Electron Fractograph of Ti-6Al-4V Alloy Fractured in Anhydrous Methanol 3450X

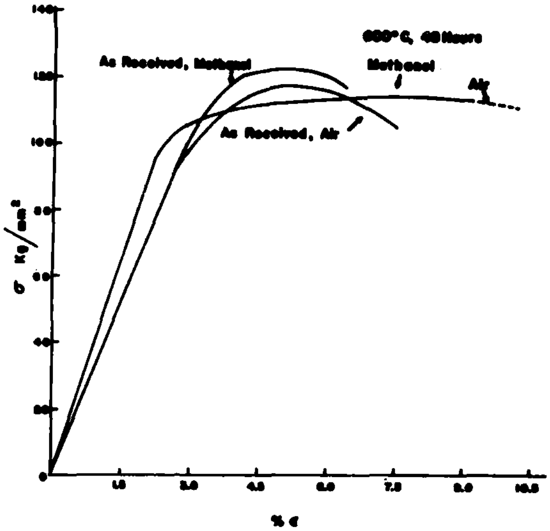

Figure 3. Stress-Strain Curve in Air and Methanol

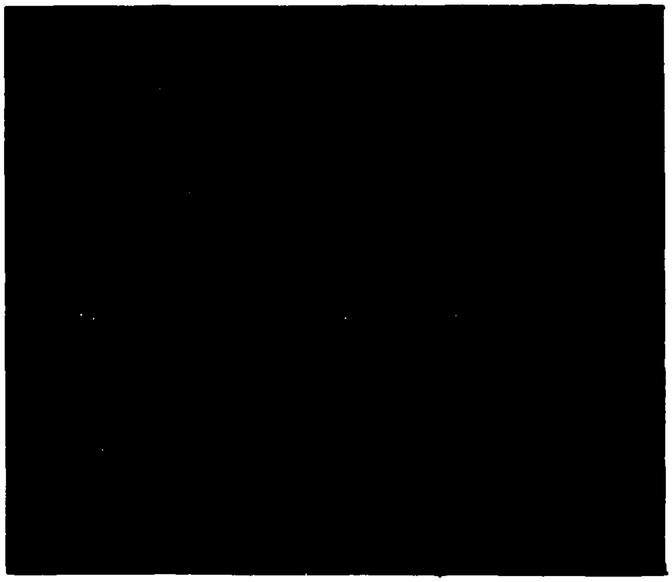

Figure 4. Electron Fractograph of Ti-6Al-4V Fractured in Air 3450X

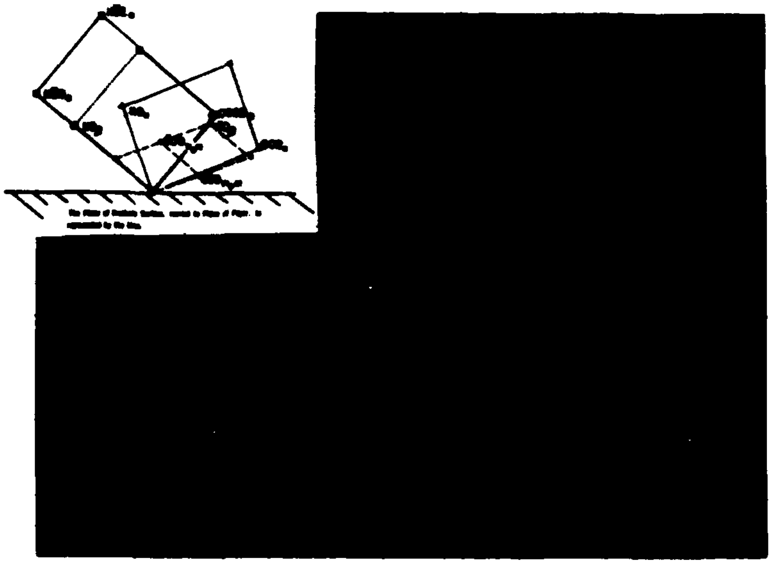

Figure 5. High Resolution Electron Diffraction Pattern of the Fracture Surface of a Specimen Tensile Tested in Anhydrous Methanol

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