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ON HYDRIDING OF TITANIUM

by

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THE INFLUENCE OF A SURFACE OXIDE FILM ON HYDRIDING OF TITANIUM

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INTRODUCTION

Titanium, zirconium, and many of their alloys are susceptible to hydrogen embrittlement.¹ Hydrogen can be absorbed by these metals during fabrication or exposure to free hydrogen in either a gas or liquid environment. Hydrogen absorption leads to the formation of hydrides usually resulting in a degradation of preferred mechanical properties, notably of toughness, with occasional catastrophic brittle failure under stress. The severity of the embrittlement is related to the volume fraction, distribution, and orientation of hydride formed. The effects of the texture of fabricated products, and of applied stress on the orientation of hydride precipitates in zirconium and titanium alloys have been evaluated previously.²⁻⁶

Titanium and zirconium alloys form oxide films that are stable in hydrogen.⁷ Thus, the permeation rate of hydrogen through the oxide film must influence hydrogen absorption by these alloys. In the case of Zircaloy-2, oxide films formed by chemical polishing have been shown to retard hydrogen absorption significantly.^{8,9} The permeation rate of hydrogen through zirconium oxide is known,¹⁰ and the effects of zirconia films on the rate of absorption of hydrogen in zirconium and on the time required to develop hydride precipitates may be estimated.

Evidence that oxide films also block hydrogen absorption in titanium has been obtained from investigations of the reaction of titanium in gaseous hydrogen^{11,12} and from stress corrosion studies.¹³ Quantitative assessment of the effect of an oxide film

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on hydrogen absorption by titanium has not been made, however, since the diffusivity of hydrogen in titania was not established until recently when tritium diffusion in rutile single crystals was measured.¹⁴ These data allow the reaction between titanium covered by a thin oxide film and hydrogen to be determined by solving the diffusion equation for a solid with a low diffusivity surface film¹⁵ using the measured diffusivities of hydrogen in rutile¹⁴ and alpha-titanium.^{16,17}

Oxide films that form on titanium at temperatures above 300°C have been identified by electron and x-ray diffraction as the rutile form of titanium dioxide.^{18,19} Rutile also forms on some binary titanium alloys and most likely is the oxide on commercial titanium alloys. During the oxidation of titanium in room temperature air, the oxide film (probably also rutile) grows rapidly to ~20 Å in thickness during the first several hours and then more slowly²⁰ and obtains a final thickness of about 30-40 Å after about one month. Growth rates and final film thicknesses are greater at higher temperatures.

Above 400°C, oxygen diffusion into the base metal becomes significant as shown by changes in the kinetics of the titanium-oxygen reaction,^{21,22} where the oxygen solubility becomes relatively high. As oxygen is known to decrease the thermodynamic activity of hydrogen in alpha-titanium,^{23,24} solution of oxygen in titanium (as could occur during film growth) would itself reduce hydrogen absorption, in addition to the effect of the oxide film *per se*.

Hydrogen absorption may also be affected by the textures which develop in titanium during mechanical working. These textures lead to a preferred orientation in the oxide film because of the epitaxial relation that exists between alpha-titanium and the oxide.²⁵ Hydrogen diffusion in rutile is both relatively slow and highly anisotropic; therefore, the preferred orientation of the oxide film may lead to widely differing absorption rates in various areas of the metal depending upon the oxide orientation. These factors, metal texture, film orientation, and anisotropy in hydrogen diffusion, are believed to explain the generally low absorption rate in titanium alloys and to account for most of the observed variability in hydriding susceptibility.

MECHANISM FOR HYDROGEN ABSORPTION

Absorption of hydrogen by a hydride-forming metal covered by an oxide film may be divided into three stages. First, a transient stage controlled by the properties of the oxide during which the

hydrogen penetrates to the oxide-metal interface. Second, a further transient during which hydrogen diffuses into the metal. This stage is controlled by hydrogen diffusivities in both the oxide and metal and by the oxide thickness. This stage ends when the hydrogen concentration in the metal at the oxide-metal interface reaches the saturation concentration for the temperature of the test. The third stage, formation of a hydride layer, then begins with nucleation and growth of the hydride at the oxide metal interface. However, if the metal can supersaturate with hydrogen, because precipitation of the hydride is inhibited, layer growth may not occur. Such effects have led to a distributed hydride precipitation in Zircaloy under some conditions.²⁶ This type of precipitation is unusual; therefore, initiation of hydride precipitation in titanium will be assumed to proceed by layer growth at the metal-oxide interface.

The diffusion equation for absorption into a substance through a membrane or surface film of low permeability from a region at constant concentration has been solved for sheets, infinite cylinders, and spheres.^{15,27} The boundary condition, referred to as a surface resistance or surface evaporation condition, relates the rate of absorption per unit area of the metal surface, or flux, to the difference between the actual concentration, C , and the saturated concentration, C^* , at that surface and may be written as:¹⁵

$$D \nabla C = \alpha(C^* - C).$$

where:

α = proportionality constant, D'/δ

D' = diffusivity of film, cm^2/sec

δ = film thickness, cm

This analysis appears applicable to hydrogen absorption in titanium up to the commencement of hydride precipitation. After this, a more complex situation exists which involves multilayer diffusion and a moving hydride-metal interface.

The solution to the diffusion equation for a sheet with the above boundary condition is:

$$\frac{C}{C^*} = 1 - \sum_{n=1}^{\infty} \frac{2L \cos(\beta_n x/l) \exp(-\beta_n^2 Dt/l^2)}{(\beta_n^2 + L^2 + L) \cos \beta_n}$$

$$L = l\alpha/D$$

l = half thickness ($t_{1/2}$), cm, of the sheet

D = diffusivity of absorbent, cm^2/sec

x = dimension variable, cm, for the sheet measured from the center-line

t = time, sec

and β_n is obtained from roots of $\beta_n \tan \beta_n = L$

Derivation of this expression assumes that the concentration of diffusant at the outer surface of the film is constant; i.e., the flux through the film equals the flux into the metal surface.

Several additional assumptions implicit in the application of this expression to hydrogen absorption by oxide covered titanium are:

- The oxide film is the rutile crystalline form of titania
- Properties of the film and bulk oxide are the same
- The film is a nonreactive permeable membrane
- The film has grown epitaxially on the titanium surface
- The film has a uniform orientation and is free of short circuit diffusivity paths.

Estimates of the time required for the metal surface to reach saturation were made from the first term of this expression and data on hydrogen diffusivity in rutile¹⁴ and alpha-titanium,^{16,17} which are shown in Figure 1. Similar estimates could be obtained through application of heat transfer charts that incorporate a film coefficient.²⁸ Although the experimental values for hydrogen diffusivity in titania were obtained using tritium, these data were converted to protium diffusivity, assuming the inverse-square-root of mass relation between diffusivity and isotopic mass. Estimates of the time for surface saturation are shown in Figure 2 for the case of a sheet, $l = 0.0127$ cm, with a 10^{-6} cm thick oxide film. This value of l was chosen for comparison with experimental data discussed later. An oxide film 10^{-6} cm thick is slightly thicker than a normal air-formed film at room temperature. The oxide films were considered to have a uniform orientation with either the c- or a-axis perpendicular to the surface, as indicated in Figure 1.

The predicted reaction time is very dependent upon the oxide film orientation with respect to the titanium sheet (Fig. 2). For example, at room temperature in about one month a surface film of gamma-hydride would begin to form under an oxide with its c-axis

perpendicular to the surface, whereas over 3 years would be required to reach the same condition if the oxide film had its a-axis perpendicular to the sheet. From the expressions for C/C^* , the elapsed time to surface saturation will increase for thicker sheets because of the larger available volume for hydrogen absorption in the high diffusivity medium.

EXPERIMENTAL RESULTS

Results of hydrogen absorption experiments in Ti-5Al-2½Sn alloy are shown in Figure 2. Specimens 0.0127-cm thick were exposed in a tube furnace, five at a time, to flowing hydrogen gas at one atmosphere pressure. The hydrogen was purified by passage through a palladium-silver alloy thimble. Oxide film thicknesses were not measured, but were probably less than 10^{-6} cm. Reaction times for temperatures of less than 200°C were estimated by noting a rapid absorption of hydrogen (decrease in exhaust flow) and subsequent spalling of the specimen due to hydride formation. Not all specimens had reacted when the tests were stopped after 77 to 120 hours at 71°C and 840 hours at room temperature. At 146°C, 39 of the 40 specimens showed evidence of hydride when they were removed from the furnace.

DISCUSSION

The predicted reaction times, shown in Figure 2, are believed to be generally applicable to the Ti-5Al-2½Sn alloy, as well as to pure titanium, because the measured hydrogen diffusivity in Ti-5Al-2½Sn at 70°C²⁹ is consistent with extrapolated data for alpha-phase titanium. Oxide films on the alloy are expected to be rutile, although perhaps of a slightly different composition.

At these temperatures (less than 200°C), the observed reaction times are compatible with the model if the reaction is assumed to begin as a consequence of hydrogen attack in areas with c-axis orientation as expected along the specimen edges. This appears to be the location of the attack (Figure 3).

Predicted reaction times for hydriding titanium cover a wide span because of the large anisotropy in hydrogen diffusivity in rutile, which serves as a protective film. Diffusion through rutile is the dominant factor in predicting reaction times. Although more accurate data on hydrogen diffusivity in alpha-titanium at low temperatures may improve the estimates, the observed reaction times appear to be consistent with the mechanism, and the large dependence on oxide orientation has been established.

The predicted reaction times are strictly applicable to unalloyed alpha-titanium. Further information on the effects of hydrogen diffusivity would be needed to refine the estimates for the several commercial alloys now in use. However, good agreement between estimated and observed reaction times in Ti-5Al-2 $\frac{1}{2}$ Sn show that the proposed mechanism is applicable to this alloy.

Cold rolled titanium sheet has a strong texture with the basal plane (0001) rotated 40 degrees toward the transverse direction about an axis in the rolling plane, and the (10 $\bar{1}$ 0) direction is parallel to the rolling direction.³⁰ Hot rolled sheet has the same texture but with a larger spread. Consequently, the oxide film is likely to be preferentially oriented with its a-axis within 40 degrees of perpendicular to the plane of the sheet. A film of this orientation is less permeable to hydrogen than one with the c-axis perpendicular to the surface; therefore, rolled sheet might be expected to be relatively resistant to hydrogen absorption and subsequent embrittlement, except in scratched or cut areas, such as the edges, where the metal texture and hence, oxide orientation are disturbed. These disturbed areas are the regions where hydriding attack is generally initiated.

In many applications titanium is welded. The orientation of the weld metal and of its oxide film can be expected to differ from that of the remainder of the structure and should contain areas oriented so as to maximize hydrogen absorption. The observed tendency for hydrogen attack in the vicinity of welds thus may be attributed to enhanced hydrogen penetration because of an altered film orientation, rather than to microstructural changes or contamination resulting from welding as has been suggested.³¹ This conclusion indicates that suppression of hydriding through control of heat treatment is not feasible, because subsequent fabrication would alter the protective film in localized areas and thereby increase hydriding susceptibility.

Another variable that may influence hydrogen attack is the extent of oxygen solution in the base metal. Diffusion of oxygen into alpha-titanium is not very deep, except at temperatures above 400°C., because of the low oxygen diffusivity.^{21,22} However, the oxygen concentration in the metal at the metal-oxide interface approaches a limiting value of 26 atom % at high temperatures,¹⁹ and could be significant at lower temperatures.

Studies of the Ti-O-H system^{23,24} show that for a given hydrogen pressure, dissolved oxygen reduces the solubility of hydrogen in titanium. Furthermore, the stability of the hydride phase relative to the alpha solid solution of hydrogen is reduced by the presence of oxygen. Therefore, a larger hydrogen content and a higher pressure are required for hydride precipitation in

alpha-titanium that contains oxygen than in oxygen-free titanium. Thus, an oxygen rich alpha-titanium layer, as well as the oxide film itself, may contribute to the protection of the base metal from hydrogen embrittlement.

The variations in oxide films caused by variations in specimen preparation techniques, specimen textures, exposure atmospheres, and other experimental variables, must contribute significantly to the wide differences in the hydriding behavior of titanium alloys found by various investigators.^{11, 12, 31} This study indicates that any investigation of titanium-hydrogen reactions must include an investigation of the effects of experimental variables on the protective titania film if meaningful interpretations of the data are to be made.

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