

Volume 7 Preprint 7

HYDROGEN PERMEATION AND DIFFUSION COEFFICIENT MEASUREMENT IN GAMMA TITANIUM ALUMINIDES

H. A. Estupiñan, I. Uribe and P.A. Sundaram§*

Corrosion Research Group

School of Metallurgy and Materials Science

Universidad Industrial de Santander

AA 678, Bucaramanga, Colombia

§Department of Mechanical Engineering

University of Puerto Rico

Mayaguez, PR 00680, USA

* Corresponding author (psundaram@me.uprm.edu; Tel: 1-787-832-4040; Fax: 1-787-265-3817)

ABSTRACT

The permeation of hydrogen in gamma titanium aluminides was studied using the ASTM G148 standard. Thin disk-shaped samples of gamma titanium aluminide with three different microstructures were appropriately prepared and cathodically charged in an aqueous 0.1 N NaOH solution using the Devanathan–Stachurski cell. The permeation current was monitored as a function of time. The permeation of hydrogen in gamma titanium aluminides appears to be relatively slow. Permeation parameters were calculated using the time lag criterion (non-steady state lag). Values of the apparent diffusion coefficient of hydrogen in gamma titanium aluminide varying from $3.75 \times 10^{-10} \text{ cm}^2/\text{s}$ to $1.87 \times 10^{-11} \text{ cm}^2/\text{s}$ were obtained. This slight variation is attributed to differences in microstructure.

Keywords: titanium alloys, hydrogen, permeation, diffusion

INTRODUCTION

The potential of gamma titanium aluminides (γ TiAl) in aerospace applications have been laid out earlier [1,2] and the use of hydrogen and hydrogen mixtures as fuels for reaching such high speeds has been suggested [3,4]. For such applications to be viable, the interaction between hydrogen and γ TiAl has to be understood clearly. An important implication of this proposed application is the degree of hydrogen permeation in these materials. Some information on the solubility of hydrogen in γ TiAl is available [5,6] and the diffusion coefficient of hydrogen in these alloys has been estimated [7]. However, a permeation study as such has not been reported in literature. This paper reports the results of baseline data of hydrogen permeation in γ TiAl and consequently the calculation of the diffusion coefficient of hydrogen. The same parameters for Ti6Al4V alloy are also reported for comparison.

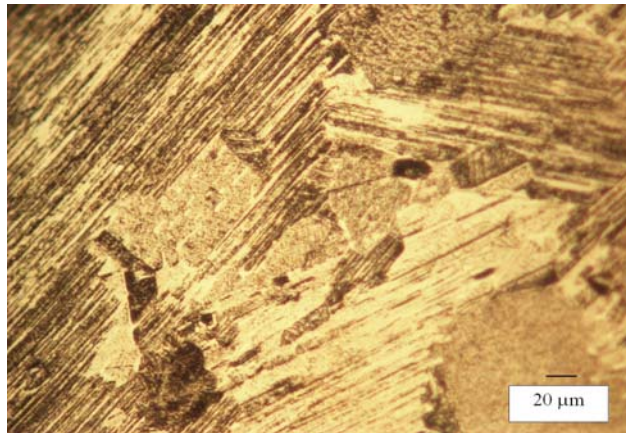
EXPERIMENTAL

A computer-controlled potentiostat/galvanostat (Galvpot 201H) was used to carry out the permeation experiments in an electrochemical cell with three electrodes: a graphite counter electrode and a saturated Ag/AgCl reference electrode for each cell compartment and the γ TiAl sample which serves as the working electrode mutual to both compartments. The nominal compositions of the γ TiAl alloys used in this research are given in Table 1 and their respective microstructures in Figure 1.

Table 1. Nominal compositions and microstructural descriptions of the Ti-based alloys.

Designation	Nominal composition	Microstructural description
RP/M	Ti-48Al-2Cr-2Cr (at.%)	80 vol.% lamellar with $\sim 300 \mu\text{m}$ colony size and 20 vol.% blocky gamma grains
SDFL	Ti-46.5Al-4(Cr,Nb,Ta,B)	100 vol.% lamellar with $\sim 150-$

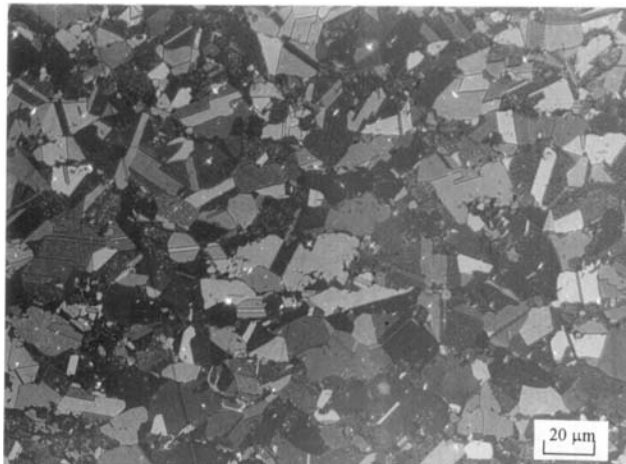
	(at.%)	200 μm colony size
SPA	Ti-46.5Al-4(Cr,Nb,Ta,B) (at.%)	Blocky gamma grains with 20 μm grain size with 8–10 vol. % α_2
Ti6Al4V	Ti-6Al-4V (wt.%)	$\alpha + \beta$ with equiaxed α grains with intergranular β



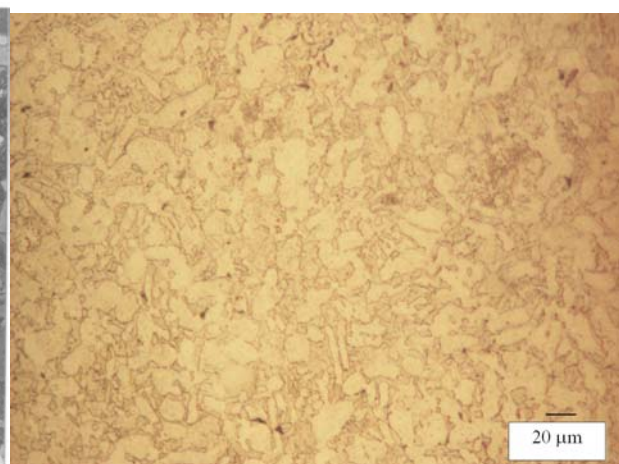
(a)



(b)



(c)



(d)

Figure 1. Typical microstructures of (a) RP/M, (b) SDFL, (c) SPA and (d) Ti6Al4V. See Table 1 for descriptions of microstructures.

The hot isostatically pressed powder based γ TiAl alloy (RP/M) and Ti6Al4V alloy were received in the form of 25 mm and 50 mm diameter rods respectively. From these materials, small cylinders 10 mm in diameter and 15 mm in length were machined using electric discharge machining (EDM). These cylinders were cut into 1 mm thick disks and the surfaces to be exposed to electrolytic charging were ground using 600 grit paper until the disk thicknesses reached about 0.3 mm. The sheet γ TiAl alloys were obtained in 1 mm thick sheets in the primary annealed (SPA) and designed fully lamellar (SDFL) microstructural conditions. These were also cut into 10 mm diameter disks and ground with 600 grit paper to a thickness of approximately 0.3 mm. The RP/M microstructure consists of 80 vol.% lamellar with an average colony size of 300 μ m and 20 vol.% blocky gamma grains. SPA has a microstructure consisting of blocky gamma grains of about 20 μ m size and 8–10 vol. % of α_2 at the grain boundaries. SDFL has a lamellar colony size of 150–200 μ m. The Ti6Al4V alloy has a $\alpha + \beta$ microstructure with predominantly equiaxed α grains (\sim 10 μ m) with intergranular β . The electrolyte used was an aqueous solution of 0.1 N NaOH (pH=12.6) and the permeation experiments were carried out at 298 K. Other experimental details are given in Table 2. All the permeation experiments were conducted and analyzed according to ASTM G5 standard (Reference test method for making potentiostatic and anodic polarization) and ASTM G148 standard (Evaluation of hydrogen uptake, permeation and transport in metals by an electrochemical technique).

Table 2. Parameters used for the permeation experiments.

Parameters	RP/M	SPA	SDFL	Ti6Al4V
Thickness, mm	0.300	0.395	0.395	0.300
Area of H generation, mm ²	0.7	0.7	0.7	0.7
Area of H permeation, mm ²	0.5	0.5	0.5	0.5
Temperature, K	298	298	298	298

Electrolyte	0.1 N NaOH	0.1 N NaOH	0.1 N NaOH	0.1 N NaOH
pH	12.6	12.6	12.6	12.6
H detection potential, mV	150	45	155	160
H generation potential, mV	-1850	-1950	-2000	-1920
Charging time, h	12	12	12	12

Nitrogen was bubbled throughout each experiment into the electrolyte to remove dissolved oxygen. Potentiodynamic polarization experiments were first carried out to determine the initial potential for the hydrogen evolution (reduction). These same conditions were used for the permeation experiments.

Duplopoteniostatic permeation technique

This technique was originally developed by Devanathan and Stachurski [8]. In this Devanathan–Stachurski two-compartment cell, hydrogen is introduced by cathodic reduction ($H^+ + e^- = H$) in one compartment (entry side), into the sample whose hydrogen permeation is to be determined. This hydrogen evolution occurs on the entry side of this thin sample (working electrode) by adsorption (H_{ads}). The adsorbed hydrogen is then absorbed (H_{abs}) into the sample and further permeates the sample by diffusion. These hydrogen atoms diffuse out of the sample (exit side) into the second cell compartment and dissolve ($H = H^+ + e^-$) into an alkaline solution of 0.1 N NaOH. The exit side of the sample is maintained at a potential high enough relative to the reference electrode such that any reduction of hydrogen will occur only at the graphite counter electrode in the second compartment. In this way, all the electrons consumed in the process contribute only to hydrogen reduction and the Faraday equation can be then used to measure the flow of hydrogen. The resulting current due to hydrogen reduction in the anodic compartment of the

electrochemical cell is a direct measure of the hydrogen permeation through the sample (γ TiAl). This permeation current density was monitored as a function of time. The current density at steady state is taken as the reference from which the required time parameters are calculated. The time parameters were calculated using the time lag criterion (non-steady state lag), which takes into account the time at which the permeation current reaches 63% of its maximum value. The apparent coefficient of diffusion of hydrogen in the sample can be determined by any one of the following expressions:

$$D = s^2/6 t_{\text{lag}}$$

$$D = s^2/15.3 t_b$$

$$D = s^2/2 t_0$$

Where,

t_{lag} is the time needed to reach 63% of the maximum steady state current density

t_b is the breakthrough time, obtained by extrapolating the linear part of the transient permeation current to $i = 0$

$1/t_0$ is the slope of the plot of $\ln(P(t) - P_{\text{max}})/P_{\text{max}}$ versus t

$S = (I_{\text{max}} \times s)/(F \times D)$, is the apparent solubility of hydrogen (mol H/m³)

D is the apparent diffusion coefficient of hydrogen (m²/s)

$P = (I_{\text{max}} \times s)/F$, is the permeability of hydrogen (mol H.m²/m.s)

S = sample thickness (m)

F is the Faraday constant

These permeation experiments were carried out for γ TiAl. For comparison, the same experiments were repeated for Ti6Al4V.

RESULTS AND DISCUSSION

The interaction of hydrogen with gamma titanium aluminides has been extensively studied from the perspective of hydride formation [9–12]. Although, the characteristics of this hydride have been documented well, the value of the diffusion coefficient of hydrogen in γ TiAl has been reported only once in literature [7] using an electrochemical technique based on cathodic charging [13]. A fundamental study of the permeation of hydrogen in this material at room temperature has not been attempted.

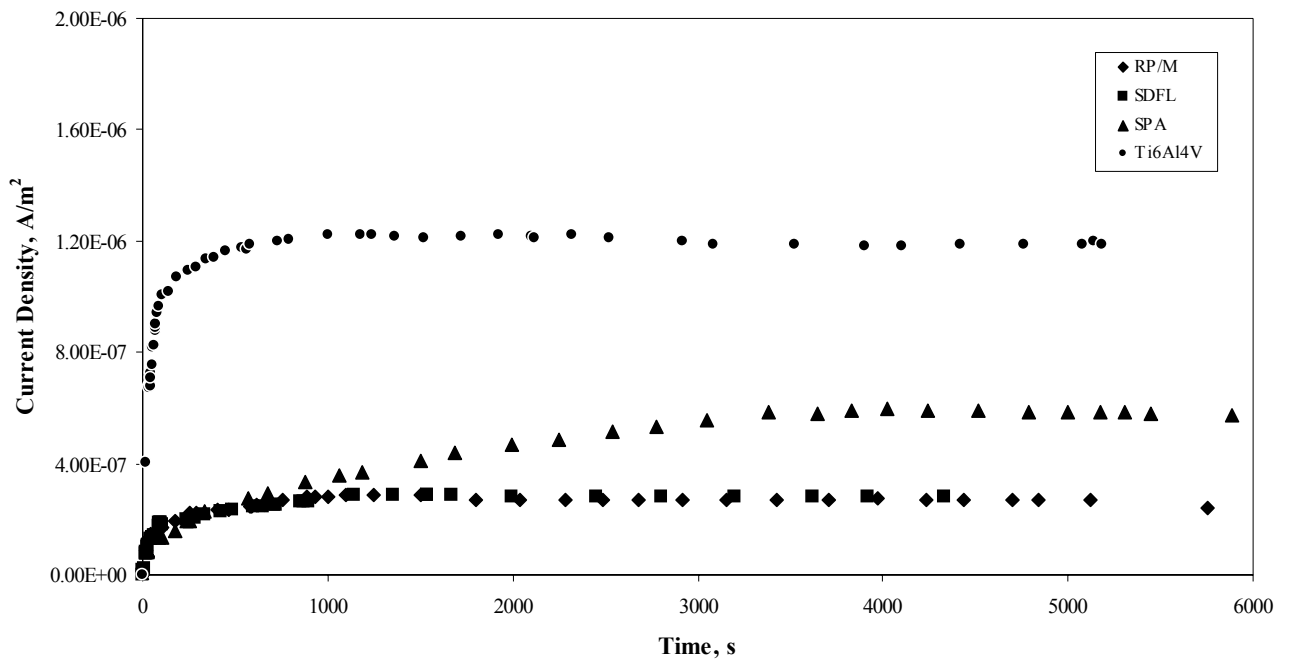


Figure 2. Permeation plots for the gamma titanium aluminides and Ti6Al4V.

Figure 2 shows typical permeation curves for the γ TiAl alloys and Ti6Al4V. The plots appear similar for the RP/M gamma TiAl and the designed fully lamellar (SDFL) material. Permeation is clearly slower for the primary annealed (SPA) alloy. In comparison, hydrogen permeation appears to be faster in Ti6Al4V. Table 3 summarizes the results obtained from the permeation experiments for all materials. The maximum permeation current value obtained for these titanium based alloys as a whole is very small compared to steels and the same

is true for the solubility of hydrogen in γ TiAl and its apparent permeability [14]. The apparent diffusion coefficient of hydrogen in γ TiAl varies slightly between the alloys tested. The values reported are similar to those obtained from an earlier study [7] although the electrochemical technique utilized for determining the diffusion coefficient was different [13] from the more fundamental technique used here. However, the close agreement between the diffusion coefficient values obtained from two different techniques adds credibility to the numbers reported.

The solubility of hydrogen in these materials has been determined before. Boodey et al. [15] have reported that the solubility of hydrogen in γ TiAl is very low while very large solubility values have been measured for the α_2 phase in the Ti–Al system [5]. Other studies related to solubility have also been reported [16,17]. It would be then expected that the presence and amounts of the α_2 and gamma phases in these materials would affect the permeability parameters to a certain extent. In the different microstructures of the γ TiAl alloys used in this study, the fractions of the α_2 phase and the gamma phase vary with microstructure. In the microstructures which are completely lamellar (SDFL) or with a high volume fraction of lamellae (~80 vol.% for RP/M), there is also a fraction of the α_2 phase for the compositions of the alloys in this study. For the primary annealed material (SPA), the vast majority of the microstructure is made up of blocky gamma grains while the α_2 phase (at 8–10 vol.%) is distributed at the grain boundaries and triple points. One would then expect hydrogen to permeate faster in the microstructures consisting of a larger fraction of the α_2 phase. On the other hand, the presence of the lamellar microstructure would be expected to provide easier diffusion paths for hydrogen through the lamellar boundaries. However, as noted in this study and in earlier work [7,18], the values of the apparent diffusion coefficients calculated indicate that lattice diffusion is the preferred diffusion path (see Table 3). The permeation of hydrogen in RP/M is slightly faster because of the smaller size and hence more boundary area of the lamellar colonies compared to SDFL with an average lamellar colony size of 150–200 μm . In the primary annealed SPA material, the permeation is much slower. In fact the lag time to reach maximum permeation current in SPA is much greater than for the other alloys used in this study indicating slower kinetics of hydrogen in the gamma phase. Surface entry

effects are ruled out in view of the emphasis in literature regarding the low solubility of hydrogen in the gamma phase [6,15]. The apparent solubility of hydrogen in SPA appears to be higher probably because of the relatively larger amount of hydrogen dissolved in the α_2 phase inadvertently present in the microstructure. The $\alpha+\beta$ structure of Ti6Al4V is much more amenable to the permeation of hydrogen, not because of the high solubility of hydrogen in α , but because of the presence of the open bcc structure of the β phase in this material. However, the difference in permeation in Ti6Al4V compared to the γ TiAl alloys is not that drastic since the β phase is not present in large amounts in this material.

Table 3. Summary of experimental results.

	RP/M	SDFL	SPA	Ti6Al4V
Max. permeation current density I_{\max} , $\mu\text{A}/\text{cm}^2$	0.226	0.288	0.617	1.15
Time lag t_{lag} , s	40	144	1390	46
Apparent diffusion coefficient of hydrogen, cm^2/s	3.75×10^{-10}	1.81×10^{-10}	1.87×10^{-11}	3.26×10^{-10}
Apparent hydrogen solubility, $\text{mol H}/\text{mm}^3$	0.008	0.086	1.33	0.010
Apparent hydrogen permeability, $\text{mol H}/\text{m.s}$	7.02×10^{-10}	8.95×10^{-10}	2.55×10^{-9}	3.57×10^{-10}

From Table 3, it is clear that the permeation current in Ti6Al4V is an order of magnitude greater than in the gamma titanium aluminides. An interesting phenomenon is observed in the permeation curves for all the titanium based alloys used in this study. A maximum is observed followed by a slight decrease in the permeation current as a function of time in all the alloys studied. This may be an indication of hydride formation on the entry side of the titanium

alloy samples. The latter occurrence is to be expected in titanium alloys which are highly susceptible to hydride formation. Despite the differences in the microstructures, the apparent diffusion coefficient of hydrogen in these materials as a whole is rather small at room temperature.

CONCLUSIONS

1. The permeation of hydrogen into γ TiAl is relatively slow at room temperature.
2. The apparent room temperature diffusion coefficient of hydrogen in gamma titanium aluminide varies from $3.75 \times 10^{-10} \text{ cm}^2/\text{s}$ to $1.87 \times 10^{-11} \text{ cm}^2/\text{s}$ depending on the microstructure.

REFERENCES

1. H.A. Lipsitt, Mater. Res. Soc. Symp. Proc., 39 (1985) 351.
2. Y.W. Kim, Journal of Metals, 41 (1989) 24.
3. H.G. Nelson, SAMPE Quarterly, 20 (1988) 20.
4. A.W. Thompson, in: R.H. Jones and R.E. Ricker (Eds.), Environmental effects on advanced materials, TMS-AIME, Warrendale, PA, 1988, p.21.
5. W.Y. Chu, A.W. Thompson, J.C. Williams, Acta Metall. Mater., 40 (1992) 455.
6. U. Habel, T.M. Pollock, A.W. Thompson, in: A.W. Thompson and D.R. Moody, Hydrogen effects in metals, TMS, Warrendale, PA, 1996, p.787.
7. P.A. Sundaram, E. Wessel, H. Clemens, H. Kestler, P.J. Ennis, W.J. Quadakkers, L. Singheiesr, Acta Mater., 48 (2000) 1005.
8. M.A.V. Devanathan, Z. Stachurski, Proc. R. Soc. London, A279 (1962) 90.
9. D. Legzdina, I.M. Robertson, H.J. Birnbaum, Mater. Res., 6 (1991) 1230.
10. Y. Combres, S. Tsuyama, T. Kishi, Scripta Metall. Mater., 27 (1992) 509.
11. J. Gao, Y. Wang, W. Chu, C. Hsiao, Scripta Metall. Mater., 27 (1992) 1219.
12. A. Takasaki, Y. Furuya, K. Ojima, Y. Taneda, Scripta Metall. Mater., 32 (1995) 1759.
13. C.J. Wen, C. Ho, B.A. Boukamp, I.D. Raistrick, W. Weppner, R.A. Huggins, Int. Met. Rev., 5 (1981) 253.
14. J.P. Hirth, Met. Trans., 11A (1980) 861.
15. J.B. Boodey, M. Gao, W. Wei, R.P. Wei, Gamma Titanium Aluminides, TMS, Warrendale, PA, 1995, p.101.
16. A. Takasaki, Y. Furuya, K. Ojima, Y. Taneda, J. Alloys Comp., 225 (1995) 299.

17. P.A. Sundaram, W.J. Quadakkers, L. Singheiser, J. Alloys Comp., 298 (2000) 274.

18. O.S. Abdul-Hamid, R.M. Latanision, in: A.W. Thompson and D.R. Moody, Hydrogen effects in metals, TMS, Warrendale, PA, 1996, p.205.