THE EFFECT OF HELIUM AND OXYGEN
ON THE HYDRIDING OF TITANIUM SPONGE

Effet de l’hélium et de l’oxygène
sur l’hydruration de la mousse de titane

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RESUME

On a étudié l'effet de l'hélium et de l'oxygène sur la réaction de l'hydrogène avec de la mousse de platine activée. On a employé de l'hydrogène avec diverses quantités d'hélium et/ou d'oxygène, d'une part dans un système d'hydruration statique et d'autre part dans un système dynamique où l'on a fait circuler le gaz sur le titane. On a constaté que les concentrations d'oxygène allant jusqu'à 0,6% en volume n'ont aucun effet sur la vitesse de la réaction d'hydruration tandis que les concentrations d'hélium de ≥ 1% ralentissent beaucoup la réaction dans un système statique. En faisant circuler du gaz sur le métal, on empêche l'hélium d'avoir cet effet. Les résultats obtenus montrent que les traces d'impuretés d'oxygène dans les mélanges d'hélium et d'hydrogène ne sont pas à l'origine des effets cinétiques observés.

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ABSTRACT

The effect of helium and oxygen on the reaction of hydrogen with activated titanium sponge has been studied. Hydrogen gas with various amounts of helium and/or oxygen has been used in both a static hydriding system and in a dynamic system where the gas was circulated over the titanium metal. It has been shown that oxygen concentrations of up to 0.6 volume % have no effect on the rate of the hydriding reaction, while He concentrations ≥ 1% slow the reaction significantly in a static system. Circulation of the gas over the metal prevents this helium effect. The results show that trace oxygen impurities in helium-hydrogen mixtures are not responsible for the observed kinetic effects.
Introduction

The successful immobilization of tritium as a metal tritide requires that pure tritium gas (or an isotopic hydrogen mixture) be used. Tritium decays to helium-3

\[
\begin{align*}
3^1\text{H} & \rightarrow 3^2\text{He} + e^- , \text{ with a half-life of 12.35 years.}
\end{align*}
\]

Earlier investigations (Holtslander and Yaraskavitch, 1980) have shown helium gas to inhibit the absorption of hydrogen by titanium sponge. The observed decrease in reaction rate has been attributed to helium "blanketing" of the gas-metal boundary (Carlson, 1976). Our earlier work has shown that circulation of the gas over the reaction metal (dynamic hydriding) substantially reduces this effect.

Cox and Ling (1981) have suggested from their studies of the hydrogen cracking of zirconium that the apparent inhibiting effect of helium might be due to oxygen impurities rather than the helium. The effect of oxygen on the hydrogen-metal reaction is well known (Blackledge, 1968). An oxide film present on the surface of zirconium and/or titanium, in particular, or formed as a result of oxygen as an impurity in the hydrogen will inhibit the metal-hydrogen reaction, requiring the use of a higher hydriding temperature or increasing the induction time for hydriding.

The laboratory studies described in this report were undertaken to answer the question of whether the decreased hydriding rate was due to helium, or to oxygen present in the helium as an impurity.

Experimental

Titanium hydrides were prepared by direct combination of hydrogen with the metal in a 105 mL quartz reaction vessel. Figure 1 is a schematic of the system used for both the static and dynamic reactions. The titanium sponge used was -3/8+10 mesh, obtained from Alfa Products, Ventron Division (Danvers, MA). Sample weight was between 4.9 and 5.2 g (0.103 - 0.108 moles).

To activate the metal surface, the samples were vacuum annealed by heating to 600°C in a small tube furnace for 90 minutes. Temperatures were measured by a Chromel/Alumel thermocouple located on the exterior surface of the reaction vessel. Before heating, the apparatus was evacuated to at least 5 x 10^{-2} Pa. Final pressures attained at the annealing temperature ranged from 2 x 10^{-2} to 6 x 10^{-2} Pa.

When the reaction vessel had cooled to room temperature, the hydriding system, excluding the reaction vessel, was flushed with H_2 and the loop filled with the desired gas mixture (H_2, He, O_2). The gases
FIGURE 1: SCHEMATIC OF APPARATUS
were mixed by circulation through the loop using a metal bellows pump. For
analysis of gas mixtures containing less than 1000 μL O₂/L, some of the
gas was then directed to the electrolytic oxygen meter (Model 76,
Anacon Ltd., Maidenhead, England). Oxygen concentrations above 1000 μL/L
were calculated from the amount of O₂ added to the reaction system.
Hydrogen gas was purified by passing it through a hot palladium-silver
alloy membrane. Helium (Air Products, 99.995% purity) was purified in some
reactions by passing it through a hot titanium getter bed (≈750°C). Oxygen
(Air Products, 99.996% purity) was used directly. The initial gas pressure
in the loop was between 102.4 and 109.6 kPa for all reactions. In the
static reactions the gas was simply admitted to the evacuated reaction
vessel; for dynamic reactions the gas was admitted and continuously
circulated through the metal bed.

Since all volumes were calibrated, the reaction was followed by the
change in pressure in the system. The hydrogen-titanium ratios were calcu-
lated from the weight of the metal samples and pressure-volume measurements
of the amount of gas absorbed. In reactions with He and O₂ present, it
was assumed that the pressure decrease was due only to hydrogen absorptions.
Oxygen levels were low enough not to affect the calculated hydrogen-
titanium ratio. Maximum hydrogen-metal ratios were limited to 1.75 - 2.00
by the choice of sample size and initial gas pressure.

Results and Discussion

The effects of He and O₂ on the hydriding reaction are discussed
for both static and dynamic (circulating) systems. A comparison of the
change in the hydrogen-titanium ratio per unit time was used to assess the
impurity effects on the hydriding reaction. The "rate" of the reactions is
discussed in reference to this change.

The initial He concentration in the gas phase ranged from 1 to 13
volume percent. This concentration increases as the reaction proceeds and
hydrogen is absorbed. Initial oxygen concentrations ranged to 12 000 μL/L
(1.2 volume %), but the O₂ concentration also changes as the reaction
proceeds. Thus concentrations quoted refer to the initial concentration
unless otherwise stated. The lowest measured O₂ level achieved was
8 μL/L; residual oxygen levels ranged from 8 to 40 μL/L.

Effect of Helium on Hydrogen-Metal Reactions

The effect of helium concentrations ranging from 1.1% to 13.1% on
the static hydriding reaction is illustrated in Fig. 2. All samples were
annealed at 600°C for 90 minutes and cooled to room temperature before the
reaction. The effect of helium is apparent within the first minute of the
reaction, where the rate decreases with an increase in the initial helium
concentration. The hydrogen-titanium ratios for t = 0.5 minutes are shown
in the following table.
HYDROGEN-TITANIUM RATIO

CO

— I —

in

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— n

x

— z.

I —

c

CO

“D

O

z:

CD

m

ro

TIME. MINUTES

HYDROGEN-TITANIUM RATIO

STATIC REACTIONS OF H2-HE WITH TITANIUM SPONGE

FIGURE 2
This ratio increases slowly after the initial reaction, as indicated by the curves shown in Fig. 2. The rate of hydrogen uptake becomes relatively constant as each reaction proceeds. The results in Fig. 2 indicate a correlation between the initial reaction rate and the amount of helium present.

The effect of helium on the dynamic hydriding reaction is illustrated in Fig. 3. The hydrogen-titanium limit is indicated as calculated from the amount of titanium and hydrogen available for the reaction. The reaction with 1.4% He reached a hydrogen-metal ratio of 1.94 after six minutes. The maximum ratio of 1.76 with 11% He was reached after five minutes. Although the He concentrations varied, the initial rate (within 1.0 minutes) was very similar for all reactions. After 1.0 minutes, the hydrogen-titanium ratio ranged from 1.31 with 11% He to 1.40 and 1.45 with 1.4% He and pure H2, respectively. The results suggest that 11% He may be affecting the initial reaction; however, the range of these ratios is similar to the experimental scatter observed with reactions of pure H2 as the hydrogen-titanium limit is approached.

The experimental data obtained from reactions with pure H2 and dynamic reactions of H2 and He has been fitted to the kinetic equation $\frac{da}{dt} = k(1-a)^{2/3}$ (Sharp et al., 1966), which relates the fraction, $a$, of total product formed to the time of reaction, $t$. Integration of this equation gives $R(a) = 1-(1-a)^{1/3} = kt$. The physical significance of using the equation is that the reaction is controlled by movement of an interface from the surface inward at a constant velocity. The data shown in Fig. 3 have been plotted as $R(a)$ versus $t$ in Fig. 4 where a linear relationship results for the bulk of the reaction. The data during the initial stage of reaction may be erroneous because of the very fast reaction at this time; the reaction slows as hydrogen-titanium limit is approached with a limited amount of H2 and non-hydrided metal remaining. The average value of $k$, the rate constant, using this equation is $2.4 \times 10^{-3}$ s$^{-1}$. The data though show some tendency below $R(a) = 0.2$ and above $R(a) = 0.6$ toward the inevitable deviation below the fitted line. This kinetic expression has also been used by Ono et al. (1981) for the Mg2Ni-H2 system, who determined $k$ values of $10^{-4}$ - $10^{-3}$ s$^{-1}$, dependent on pressure and reaction temperature. The result of a similar rate constant for reactions of pure H2 and H2 with He indicates that helium is having no effect on the reaction once the gas is being circulated.

When a static reaction with helium present has essentially stopped, further H2 can be absorbed simply by circulating the gas over and/or through the metal bed. The continuation of such reactions by this method
DYNAMIC REACTIONS OF H₂-HE WITH TITANIUM SPOCE

FIGURE 3
FIGURE 4

ABSORPTION OF H2 BY Ti SPONGE -- DYNAMIC REACTIONS

- 12HE/H2
- 13HE/H2
- PUR H2

\[ R(t) = 1 - (1 - \alpha)^{1/3} \]

average \( k = 2.4 \times 10^{-3} \text{ s}^{-1} \)
is illustrated in Fig. 5. The reaction rate increases significantly with circulation, but decreases when the gas is again static in the system.

The beneficial effect of circulation on a hydriding reaction with helium present implies the helium is blocking the hydrogen access to the metal by some physical means. It is suggested that in static reactions the surface region becomes depleted in H₂ (because of H₂ absorption) and therefore enriched in He. The sponge has a rough, tuffaceous surface (ratio of B.E.T. surface area to geometric is ~600) at which the He may concentrate with minimal back diffusion. This helium-rich layer prevents transport of a sufficient quantity of H₂ from the bulk gas to the metal surface to maintain the initial reaction rate. Physical disruption of this He layer by circulation allows access of H₂ to the metal surface and thus the reaction is unaffected by the helium present.

Effects of Oxygen on Hydrogen-Metal Reactions

The results of static reactions of titanium and hydrogen with added oxygen are shown in Fig. 6. Oxygen concentrations of up to 6000 μL/L (0.6 volume %) had little effect on the reaction rate. The final ratios, reached within 10 minutes, ranged from 1.95 to 1.76. The variation in the final ratios attained may result from experimental scatter; however, the result from 0.6 volume % is out of the expected range. The lower ratio obtained is consistent with results of other investigators (Blackledge, 1968).

Reactions with 0.9 and 1.3 volume % were unsuccessful; no H₂ was absorbed with 1.3 volume % after 30 minutes, while a hydrogen-titanium ratio of only 0.07 was reached after this time with 0.9 volume % present initially.

Because titanium is an excellent getter for oxygen, much of the initial oxygen present will be removed from the gas phase as a result of this exothermic reaction (∆H°₂₉₈ (TiO₂) = -218.0 kcal/mole (Keller, 1967)). The titanium-hydrogen reaction is also exothermic (∆H°₂₉₈ (TiH₂) = -29.5 kcal/mole (Mueller, 1968)). Thus, either reaction can promote the other by increasing the metal temperature. A large amount of oxygen, though, may form sufficient surface oxide to inhibit the reaction of hydrogen with the metal. This result was observed with oxygen concentrations greater than 0.9 volume %. In the reaction with 0.92 volume % O₂ present, approximately 1% of the titanium metal could have been converted to one of the oxides (TiO, Ti₂O₃, TiO₂). As the oxygen concentration is increased, the surface oxide eventually becomes thick enough to inhibit the reaction. Small induction periods (5 - 20 s) are sometimes observed with lower oxygen concentrations and with samples that may have some surface oxide remaining after the vacuum annealing treatment.
FIGURE 5

EFFECT OF CIRCULATION ON REACTIONS OF H2-HE
FIGURE 6

STATIC REACTIONS OF H2-02 WITH TITANIUM SPONGE

TIME (MINUTES)

HYDROGEN-TITANIUM RATIO

[Graph showing the relationship between time and hydrogen-to-titanium ratio with data points for different concentrations.

- NH4 limit: 2.00 for all reactions
- Concentrations: 1000 ppm O2/L, 28 li O2/L, 910 li O2/L]
The static reactions of H₂-O₂ mixtures with titanium are compared with those of H₂-He mixtures in Fig. 7. The reactions of H₂ with 280 and 910 μL O₂/L had a reaction rate similar to that of H₂ with no added O₂. The reactions with ~1% He were very much slower. Because of the slow initial rates with helium present, the maximum hydrogen-titanium ratios were not obtained during the initial 10 minutes of the reaction. Without He present, final ratios of >1.90 were reached within eight minutes even with oxygen concentrations up to 910 μL/L. The results indicate that the observed kinetic effect is due to the presence of helium, not O₂ impurities. It is suggested that the high surface area to volume ratio of the sponge results in less inhibiting effects with oxygen present than that expected from literature reports (Mueller, 1968).

Dynamic reactions with He concentrations ranging from 8.5 to 11.8% and O₂ concentrations from 13 to 280 μL/L are shown in Fig. 8. Neither the helium nor oxygen concentrations used affected the dynamic reactions, as the initial reaction rates are very similar to those with pure H₂. The reactions shown achieved their maximum hydrogen-titanium ratio within 5-6 minutes.

Conclusions

In static hydriding reactions, the initial reaction rate and the hydrogen-titanium ratio attained in a reasonable time (<10 minutes) are both affected by the initial amount of He present. The rate and final ratio both decrease with an increase in the amount of He added. It is believed He inhibits H₂ adsorption by "blanketing" the metal surface and is responsible for the observed kinetic effects. This large He effect can be eliminated by circulating the gas.

The presence of He in dynamic hydriding reactions has little effect on the reaction and/or reaction rate. In a dynamic system, initial reaction rates are similar for pure H₂ and H₂ with He concentrations of at least 13 volume percent, the maximum impurity level studied. Final hydrogen-titanium ratios are not limited by the presence of helium, thus near completion of the reaction H₂ is still adsorbed though much of the remaining gas is He.

The rate of the hydriding reaction with O₂ present is dependent on the initial amount. Initial concentrations of up to ~6000 μL O₂/L (0.6 volume %) did not affect the reaction rate. At an increased level, oxygen inhibited both the initial reaction and the final ratio.

This study of He and O₂ effects on the reactions of titanium sponge with hydrogen indicates that helium, present as an impurity in the reaction, is responsible for the inhibited reactions and not traces of O₂ that may be present in the He.
FIGURE 7

STATIC REACTIONS OF H2-HE-02 WITH TITANIUM SPONGE
FIGURE 8

DYNAMIC REACTIONS OF H2-HE-O2 WITH TITANIUM SPONGE
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References


