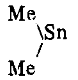
appreciably lower than 3.95 mm/s for *trans*-$Me_2Sn(acac)_2$.[15] Since for R_2SnL_4 complexes the ratio QS(trans):QS(cis) is 2:1, it is likely that in **3** an approximate cis arrangement occurs.



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Registry No. **1**, 62392-92-1; **2**, 62392-91-0; **3**, 62392-90-9; **4**, 62476-50-0; **5**, 62476-49-7; **6**, 62476-48-6; **7**, 62430-63-1; **8**, 62430-62-0; **9**, 62430-64-2; **10**, 62415-55-8; **11**, 62430-60-8.

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Mechanism for the Isothermal Decomposition of Iron Titanium Hydride

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The stoichiometric alloy FeTi has been the center of a great deal of interest as a result of its ability to absorb and desorb hydrogen under conditions which are suited to storage of the gas for use as a source of energy. Reilly and Wiswall[1] were the first to investigate the properties of hydrides of the alloy. While their primary concern was the investigation of the phase diagram of the Fe–Ti–H system, they also conducted studies of both its hydriding and its dehydriding kinetics.[2]

They found that the kinetics of the isothermal decomposition reaction appeared to be first order for most of the reaction. They also noted an apparent divergence from these kinetics at short times. It was speculated that this divergence was a result of differences in behavior between the higher and lower hydrides of FeTi.

Historically, there has been a good deal of research into the kinetics of decomposition reactions[3,4] of the type

$$\mathrm{A(solid)} \rightarrow \mathrm{B(solid)} + \mathrm{C(gas)}$$

which includes the dehydriding reaction being considered here. In general, it has been observed that such reactions are quite complicated. Usually such phenomena as nucleation of the product lattice, growth of such nuclei, and cracking of the reactant lattice due to strain from product lattice growth, as well as a variety of other such topochemical processes, can determine the kinetics of decomposition. To our knowledge, no systems other than metal hydrides exhibit apparent first-order decomposition kinetics.

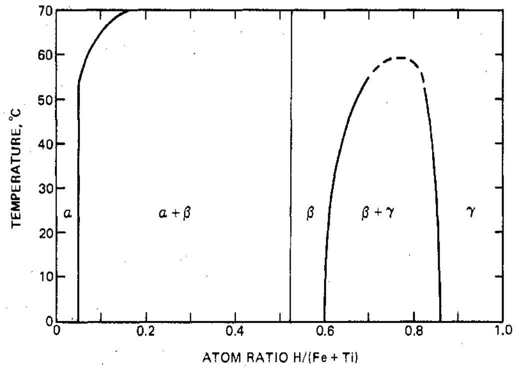

Figure 1. Phase diagram for the Fe–Ti–H system; after Reilly and Wiswall.[1]

Decomposition of iron titanium hydride under vacuum by first-order kinetics indicates that at any time each hydrogen atom has a probability of being lost to the vacuum equal to that of any other hydrogen atom. In the usual case during decomposition, the probability that any particular atom of the gas-forming species will be lost is determined by topochemical factors such as proximity to a phase boundary. Consequently, the probability of loss of a particular atom or molecule of the gas-forming species is not a constant but instead varies widely for particular atoms in the solid.

A partially decomposed sample of iron titanium hydride should contain phase boundaries (see Figure 1) and decomposition kinetics could thus be affected by them. The fact that the kinetics are not so affected indicates that some process which averages the environment of each hydrogen atom is active and of prime importance to the decomposition of this hydride. The relatively rapid diffusion of hydrogen in the hydride lattice is one such process and is the basis of the model described below. By contrast, the diffusion of the gas-forming species in other solids which undergo endothermic decompositions (e.g., carbon dioxide in carbonates, or water in hydroxides) is relatively very slow and such environmental averaging does not occur, giving rise to the normal topochemical control of decomposition.

We can postulate that a metal hydride decomposes by the series of reactions in eq 1 and 2, where the diffusion process

$$\mathrm{H(interstitial)} \xrightarrow{D} \mathrm{H(surface)} \qquad (1)$$

$$\begin{aligned} 2\mathrm{H(surface)} &\xrightarrow{k} \mathrm{H_2(adsorbed)} \\ \mathrm{H_2(adsorbed)} &\xrightarrow{k'} \mathrm{H_2(gas)} \end{aligned} \qquad (2)$$

in the first step is fast enough to average out the topochemical features which normally dominate the kinetics of decomposition reactions. For a particular metal hydride either step 1 or step 2 could be rate determining (in practice the two reactions of step 2 would be difficult to separate).

Microscopic investigation of iron titanium hydride shows that after a few hydriding–dehydriding cycles the alloy particles are split into block or platelike fragments by an extensive series of fine cracks. Characteristic dimensions of the resulting interlocked fragments are on the order 2–10 μm.[5] It therefore seems reasonable to compare the kinetics of decomposition of this system with those predicted by the equation for diffusion out of a slab.

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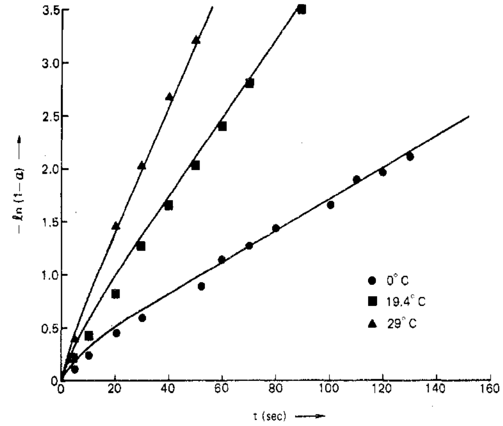

Figure 2. Decomposition kinetics of iron titanium hydride. Initial composition is $FeTiH_{1.6}$. Data from Reilly and Wiswall.[2]

Diffusion out of an infinite slab of thickness L is governed by[6]

$$\alpha = 1 - \frac{8}{\pi^2} \sum_{n\ \mathrm{odd}} \frac{1}{n^2} \exp(-n^2\pi^2 Dt/L^2)$$

where α is the reaction fraction and is equal to zero for no reaction and one for complete reaction and D is the diffusion constant.

Notice that for a sufficiently long time we can expect the first term in the summation to dominate, resulting in apparent first-order kinetics:

$$1 - \alpha \simeq \frac{8}{\pi^2} \exp(-\pi^2 Dt/L^2) \qquad \text{(for } t \text{ large)}$$

So for large t, a plot of $-\ln(1-\alpha)$ vs. t has a slope of $\pi^2 D/L^2$ and an intercept of $-\ln(8/\pi^2)$ (see Figure 2). Since D should exhibit an Arrhenius behavior ($D = D_0 \exp(-E_a/RT)$) and since L is not a function of temperature, the model predicts that a plot of D/L^2 vs. $1/T$ will yield the activation energy for diffusion. Using this approach, we find that $E_a = 7.8$ kcal/mol. This compares favorably with values for the diffusion activation energy in the β phase (FeTiH) of 7.4[7] and 6.0 kcal[8] as determined from NMR measurements.

Since the quantity L in the diffusion equation corresponds to the minimum dimension of the slab, we assume that its value here should correspond roughly to the lower values of the size distribution as seen microscopically because what would be seen would be cuts at various angles through the alloy slabs. In this case, then, we would expect $L \approx 2\ \mu$m.[5] From the slopes of the data in Figure 2, we find that $D_0 = 1.1 \times 10^{-4}$ cm^2/s. So we have

$$D = 1.1 \times 10^{-4} \exp(-3942/T)\ \mathrm{cm^2/s}$$

At 300 K this gives $D = 2.2 \times 10^{-10}$ cm^2/s which compares to an order-of-magnitude estimate of $D \approx 10^{-12}$ cm^2/s from NMR data.[8] At 343 K we get $D = 1.1 \times 10^{-9}$ cm^2/s which compares with an upper limit of $D < 10^{-8}$ cm^2/s found by inelastic neutron scattering.[9] Theoretical curves plotted with D and L as above are also shown in Figure 2.

As can be seen, the model fits the data quite well at long times and agrees qualitatively at short times although the predicted rate is slightly high. This difference probably results from differences in diffusion rate in the three phases of the Fe–Ti–H system. As a particle of the hydride decomposes, the proportions of the three different phases change as a function of time. The decomposition of one such particle could be modeled by the introduction of three separate diffusion coefficients weighted by the proportion in the particle of each of the corresponding phases. For such a decomposition, the value of the reaction fraction, α, would uniquely (assuming equilibrium) determine the phase composition by its relation to the atom fraction of hydrogen present in the particle, and the total weighted diffusion constant would be a relatively simple function of α. Unfortunately, a macroscopic sample of metal hydride powder consists of a distribution of particle sizes, and this fact greatly complicates the relation of the weighted diffusion constant to α. An analysis on this basis could be performed, but it would introduce a number of adjustable parameters into the model. While such a modified model would no doubt fit the data better, it would really add nothing to our understanding of the actual atomic processes involved. The good agreement observed with the present model probably results in part from the predominance of the β phase throughout most of the decomposition range investigated.

While the decomposition of $FeTiH_x$ is apparently controlled by hydrogen diffusion, the same is not necessarily true of the decomposition kinetics of all metal hydrides. In general, all members of a chemical class rarely decompose by the same mechanism.[3] In the case of the metal hydrides some, such as Mg_2NiH_4, exhibit too great an activation energy;[10,11] and others such as UH_3 and TiH_2 also do not display the necessary apparent first-order kinetics[12,13] at long times. These decompositions are most likely governed by recombination of hydrogen atoms at free surfaces.[12,14]

We have shown, however, that the kinetics of the isothermal decomposition of iron titanium hydride is well described by a model in which the diffusion of hydrogen out of the hydride is rate determining. The model, as presented, gives a diffusion constant in good agreement with that found by NMR methods. The mechanism of decomposition in this system is a result of the rapid diffusion of hydrogen in the solid lattice. Consequently, this mode of decomposition is probably unique to metal hydrides; however, not every metal hydride will decompose in this manner.

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