BNL--31189R
Conf-820548--3

BNL--31189R

DE82 015242

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March 1982

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This work was supported by the Division of Chemical Sciences,
U.S. Department of Energy, Washington, D.C., under Contract No.
DE-AC02-76CH00016.

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Irreversible Effects in the FeTi/H System*

J. J. Reilly, J. R. Johnson, J. F. Lynch⁺ and F. Reidinger⁺

SUMMARY

The equilibrium hydrogen absorption isotherm using annealed, strain-free FeTi, exhibits only one plateau up to a composition of FeTiH_{1.95}. However, the desorption isotherm, determined immediately after the first hydriding step, exhibits the usual two plateaux. X ray diffraction results of samples with compositions within the absorption plateau limits indicate the major phases present to be α and γ , although a small amount of β phase was always detected. Apparently the absorption isotherm represents the direct conversion of $\alpha \longrightarrow \gamma$ and β phase precipitation is almost completely suppressed. Thermodynamic quantities for this conversion are given. The results are attributed to the influence of lattice strain upon the behavior of the β_1 and β_2 phases. A practical consequence of the effect is the distortion of the pressure-composition isotherm in the β - γ region as a function of hydriding-dehydriding cycles. This is caused by an increase in H solubility of the β and γ phases and the widening of the phase composition limits as the strain increases with cycle number. However, after many hundreds of cycles there is no further significant increase in strain and the isotherm shape becomes essentially fixed and reproducible. The distortion is reversible by mild annealing.

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* This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under Contract No. DE-AC02-76CH00016.

INTRODUCTION

Recent work has suggested that the FeTi/H system exhibits an unusually large degree of irreversibility at hydrogen contents exceeding $\text{FeTiH}_{1.0}$, i.e., in the monohydride (β)-dihydride (γ) region of the phase diagram. Amano and Sasaki [1] as well as Goodell and Sandrock [2] have reported non-reproducible pressure-composition isotherms in this composition region while Reidinger, et al. [3] have suggested that the β_1 and β_2 phases are not reversible and their appearance may be due solely to lattice strain and associated defects. In this connection we note that lattice strain has also been cited as a contributory factor for the non-ideal behavior of $\alpha\text{-FeTiH}_x$ [4]. Indeed it has been shown that when lattice strain and other extraneous factors are absent the system behaves ideally over the entire solid solution composition range [5]. It is the purpose of this paper to report results of our efforts to determine, a) pressure-composition-Temperature (p-c-T) properties, at H concentrations exceeding the terminal solid solution concentration, starting with strain-free FeTi, b) confirm and extend previous results regarding the circumstances of β phase precipitation and, c) determine the cause of the unusual isotherm behavior and assess its practical consequences.

EXPERIMENTAL

The FeTi samples were obtained from a large ingot produced by TiMet Corp. of West Caldwell, N.J. Chemical Analysis gave the following composition: 46.0% Ti, 53.8% Fe, 620 ppm O, 80 ppm N, and 250 ppm C. Spectrographic analysis indicated other metals present to be Ni ($\sim 0.1\%$), Cr ($\sim 0.05\%$) and Mg ($< 0.01\%$). X-ray diffraction showed the presence only of the FeTi phase.

The apparatus and procedure for obtaining pressure-composition isotherms has been described previously [6]. Unless noted otherwise, all samples were previously activated. An activated sample is defined here as one which has been subjected to at least one complete hydriding-dehydriding cycle. In the case of FeTi this process involves a sequential expansion and contraction of ~20 volume percent which physically disrupts the solid and results in a large increase in sample surface area; for FeTi the surface area/weight ratio is typically $0.5 \text{ m}^2/\text{g}$ after activation [4]. Cycling experiments were carried out with the usual type of reactor [6] which was provided with an exterior cooling jacket. For these experiments a 10g sample was activated in the usual manner [6] after which the reactor was attached to the cycling apparatus. This consisted of a small gas manifold, pressure gauge and pressure transducer, a 500 ml gas reservoir and appropriate valving for evacuation or the addition of hydrogen. Heating and cooling of the reactor was accomplished by pumping hot or cold heat exchange fluid through the exterior jacket. Heating and cooling times could be varied as desired. In such an experiment, the reactor containing previously prepared $\text{FeTiH}_{1.8}$ was transferred to the cycling apparatus under a hydrogen pressure of ~35 atm. The manifold was evacuated and hydrogen gas was added until the pressure in the manifold and gas reservoir was ~35 atm at which point the manifold was isolated and the reactor valve was opened and the cycling process begun. The typical cycle period was 20 minutes over which the reactor temperature varied between -3°C and 110°C thereby effecting a cyclic composition change corresponding to $\text{FeTiH}_x \rightleftharpoons \text{FeTiH}_{x+1.5}$.

X-ray diffraction patterns were obtained using a Norelco diffractometer and $\text{CuK}\alpha_1$ radiation. Silicon powder (Std. Reference Material No. 640, Nat. Bureau of Standards, Washington, D.C.) was used as an internal standard.

RESULTS AND DISCUSSION

In order to examine the interaction of hydrogen with strain-free alloy a sample of FeTi was activated, outgassed at $>450^\circ\text{C}$ and annealed in situ overnight, under He, at 800°C . Such treatment relieves the cold work incurred in the activation process, as evidenced by a well resolved x-ray diffraction pattern, while maintaining the characteristic, surface area/weight ratio ($\sim 0.5 \text{ m}^2/\text{g}$) of activated FeTi. After annealing, an absorption-desorption isotherm was determined which is illustrated in Figure 1. In Figure 2 is a series of desorption isotherms which represent system behavior in the first dehydriding step using a previously activated, annealed, FeTi sample. The most striking feature of these results is that there is no evidence of second plateau in the absorption isotherm. The desorption isotherms are similar to those previously reported [6] except that the upper plateau is less sloping and the phase limits more sharply defined. The results tend to confirm the suggestion of Reidinger et al. that the intermediate hydride phases (β_1 and β_2) of this system are not completely reversible and appear as a result of strain. Their suggestion was based on X-ray diffraction data which indicated that annealed strain free $\alpha\text{-FeTiH}_x$ was converted directly into the γ phase upon the addition of hydrogen. Their original and our confirming X-ray data are listed in Table 1. It will be noted that in all such cases, however, a small amount of β phase was

detected. It is possible that its appearance is due to small regions of strained α phase surrounding previously precipitated γ phase. In any event the amount of β precipitate is too small to noticeably influence the shape of the absorption isotherm. Thus, we conclude that $\alpha\text{-FeTiH}_x$ will convert directly into $\gamma\text{-FeTiH}_x$ to the extent that it is strain free. We note there is no increase in strain in the α phase due to dissolution of hydrogen, as determined by X-ray diffraction. Nor would such be expected since the concentration of hydrogen at the solvus (in this case the $\alpha/\alpha+\gamma$ phase boundary) corresponds to $\text{FeTiH}_{.001}$ at 313K [5]. However the γ phase is highly strained due to the cold work involved in expanding the metal ~20 volume percent. When it is decomposed it does not directly revert to the α phase but rather forms an intermediate β phase which subsequently converts to the α phase. After such a cycle, which incidentally constitutes the usual activation process, the α phase is also in a highly strained state and, unless the strain is relieved by annealing, will not again convert directly to the γ phase but only via an intermediate β phase. Further, in accord with Reidinger et al. [3] and as shown in Table 1, we could only detect the β phase in samples prepared by desorption.

In Table 2 we present thermodynamic data, calculated from the slope and intercept of the van't Hoff plot shown in Figure 3, for the $\alpha \rightarrow \gamma$ conversion. Most of the data points were determined by equilibrating annealed FeTi with a measured amount of H_2 to finally result in a composition of $\text{FeTiH}_{.1}$; one point was taken from the 313K absorption isotherm (Fig. 1). This abbreviated technique is experimentally convenient, as the determination of a complete

absorption isotherm is a time consuming and tedious operation and, for the present purpose, unnecessary. We also present in Table 2 thermodynamic quantities for the $\gamma \rightarrow \beta_2$ and the $\beta_1 \rightarrow \alpha$ transitions also calculated from the plots in Figure 3. For the desorption case we have considered, on the basis of previous work [3,7] and present results that the upper plateau represents the conversion of α to β_2 and the lower plateau of β_1 to α . The present p-c-T technique is not adequate to examine the $\beta_2 \rightarrow \beta_1$ conversion. All of the data points were abstracted from desorption isotherms at a composition corresponding to the midpoint of the respective plateau. The $\gamma \rightarrow \beta_2$ and $\beta_1 \rightarrow \alpha$ values agree quite well with those obtained previously using both p-c-T [6] and calorimetric techniques [8]. While a detailed interpretation of these data must be deferred they are reflective of the degree to which thermodynamic behavior of this system is influenced by strain. This finding is not without precedent; Lynch et al. [9] noted the increased solubility of H in $\alpha\text{-PdH}_x$, where the Pd was previously activated; they attributed its cause to hydrogen interaction with dislocations created by plastic deformation of the metal concomitant with the activation process. The effect of strain upon the behavior of $\alpha\text{-FeTi}$ has already been cited. Flanagan and Clewley [10] have recently discussed hysteresis in metal hydride systems and have constructed a quantitative model which accounts for it through the production of dislocations as a result of the strain incurred in the hydriding-dehydriding process. In the present instance the situation, though certainly related, seems more complicated, since it appears that the intermediate β_1 and β_2 phases are, themselves, products of

strain. Their irreversible character is further underscored by evidence indicating that $\beta 1$ can only be produced by approaching equilibrium from one direction, i.e., by decomposing previously formed $\beta 2$ hydride and not by addition of hydrogen to α -FeTiH_x [3].

While a discussion of the mechanism of the appearance of the β phases is beyond the scope of this paper the results so far presented permit us to suggest the reason for the unusual behavior noted by Amano and Sasaki [1] and Goodell and Sandrock [2]. They have reported a gross change, as a function of hydriding and dehydriding cycles, in the pressure-composition desorption isotherm in the γ - β region of the phase diagram. The change is in the direction of lower hydrogen content and higher pressure; the upper plateau is not only shortened but raised to a higher level indicating decreased γ phase stability. Since the effective hydrogen storage capacity may be reduced, this behavior bears directly on the potential of FeTi and similar materials (TiFe_{1-x}Mn_x behaves similarly [2]) as practical and attractive hydrogen storage compounds. We have confirmed their results, as shown in Figure 4, which illustrates a family of desorption isotherms obtained after subjecting the FeTi sample to the indicated number of hydriding-dehydriding cycles and a final equilibration at 0°C and 65 atm pressure. There is a rapid initial distortion of the isotherm per cycle in the first few cycles. The effect, however, decreases as the cycles increase, until, after many hundreds of cycles, the isotherm shape becomes almost independent of cycle number. This latter behavior was also noted by Amano and Sasaki [1]. It is indicative of a strain related effect, e.g., Flanagan and Clewley [10] note that the dislocation density in metals reaches a

saturation value which will remain constant despite continued cold working and further plastic deformation. The distortion of the isotherm is reversible by annealing the FeTi sample after the dehydriding step, as shown in Figure 5. Absorption isotherms are similarly distorted after cycling as shown in Figure 6. These data were obtained with an FeTi sample which had previously undergone 1564 hydriding-dehydriding cycles. It is noteworthy that the 313K isotherm exhibits no semblance of an upper plateau and it is quite apparent that the stability of the γ phase has decreased.

From the above we are led to conclude that the change in behavior upon cycling is due to lattice strain and associated defects produced in the alloy by the cold work of expansion and contraction concomitant with each hydriding-dehydriding cycle. Usually strain manifests its presence by an increased hydrogen solubility and a tendency to widen single phase composition limits due to the interaction of hydrogen with dislocations [9]. It is likely, both from X-ray diffraction and p-c-T data, that a similar mechanism, involving the β_1 and β_2 phases, is operating in the present instance. However, the decrease in stability of the γ phase remains puzzling; in the case of the Pd/H system, β phase stability is unaffected by strain [9]. In any event the overall result is a reduction in the length of the miscibility gap and a distortion of the upper plateau in the direction of higher pressure. Finally, it becomes very difficult to define any miscibility gap at all between the β and γ phases as the number of cycles increase and both X-ray and p-c-T data suggest that there is almost a continuous phase transition from $\beta \rightarrow \gamma$ and $\gamma \rightarrow \beta$ after many cycles. Eventually, the system reaches a saturation value

with respect to strain and the shape of the desorption isotherm becomes insensitive to cycle number. This latter point is of practical importance since it indicates that, while the effective hydrogen storage capacity of FeTi will be reduced from the maximum initially possible, it will eventually reach a steady state value and remain constant. Annealing of course reduces strain and, to the extent of such reduction, the isotherm recovers. We see no discrepancy between our results and those of Goodell and Sandrock [2]. We believe the more severe and accelerated effect they observe, particularly in relation to maximum H content, is due to the more moderate conditions of temperature (25°C) and hydrogen pressure (60 atm) they adopted for the hydrogen charging step; this point is well illustrated by the absorption isotherms in Figure 6. As far as a practical limit on the hydrogen storage capacity is concerned, we estimate that under conditions approximating our own of temperature, pressure and cycle period, an effective storage capacity equivalent to $\text{FeTiH}_{1.5}$ should be easily maintained independent of cycle number.

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ACKNOWLEDGMENT

The authors wish to thank Prof. H. Brodowsky of the University of Keil for helpful discussions and Mr. S. Bookless for his experimental assistance.

TABLE 1. Phase Composition of FeTiH_x

Exp	x in H _x	Phases ¹	Strain ² Relief	Cycles ³	Mode of Preparation		Remarks
			°C		Absorb	Desorb	
1	0.34	α, γ (β)	800	0	X		
2	0.59	α, γ (β)	800	0	X		
3	1.26	α, γ (β)	800	0	X		
4	1.84	γ	800	0	X		
5	1.19	β2, α	None	3	X		
6	1.22	β1	None	6		X	
7	1.54	γ, β2	None	8		X	
8	1.12	α, γ (β2)	800		X		from [3]
9	1.65	γ, (β2)	800		X		from [3]
10	0.67	β2, α	450		X		from [3]
11	0.98	β1, (α)	450			X	from [3]
12	1.78	γ (β)	None	470	X		
13	1.51	β2(γ)	None	1566	X		

3 Strongest Reflections

Phase*	Composition	Location degrees 2θ		
β1 (ortho)	FeTiH _{0.94}	41.9	39.7	58.5
β2 (ortho)	FeTiH _{1.40}	40.9	39.9	58.6
γ (moncl)	FeTiH _{1.90}	38.5	40.9	43.1

*Ref. [3].

¹ Phases in () barely detectable. In some cases it was not possible to distinguish between β1 and β2.² Lists annealing temp. if strain relieved immediately preceding sample preparation.³ Refers to complete hydriding-dehydriding cycles immediately preceding sample preparation.

TABLE 2. Integral Thermodynamic Quantities/g Atom H for Phase Transitions
in the FeTi/H System at 298K

Transition	Composition, H/M ^a		ΔH kJ	ΔS J/K
	Initial	Final		
$\alpha \rightarrow \gamma$	5×10^{-4b}	0.82	-13.8(4)	-55(1)
$\gamma \rightarrow \beta_2$	0.91	0.57	15.5(8)	60(3)
$\beta_1 \rightarrow \alpha$	0.51	0.05	12.1(4)	47(1)

^a Taken from 313K isotherms unless otherwise noted; M = Fe+Ti.

^b Taken from ref. 5.

FIGURE CAPTIONS

1. Pressure-Composition isotherms using activated annealed (800°) FeTi. First hydriding-dehydriding reaction. $\rightarrow$ absorption, $\leftarrow$ desorption
2. Desorption Pressure-Composition Isotherms of activated, annealed (800°C) FeTi determined after first hydriding reaction.
3. Ln of Isotherm Plateau Pressure vs. Reciprocal Temp.; A= $\alpha \rightarrow \gamma$, B= $\gamma \rightarrow \beta_2$, C= $\beta_1 \rightarrow \alpha$.
4. Desorption Pressure-Composition Isotherms after indicated number of complete hydriding-dehydriding cycles, a=0, b=4, c=123, d=521, e=2424, f=3011.
5. Isotherm recovery after 3011 cycles followed by annealing 2 days at indicated temperature, a=no anneal, b=230°C, c=260°, d=300°C and e=350°C.
6. Pressure-Composition Isotherms determined immediately after subjecting FeTi sample to 1564 hydriding-dehydriding cycles; $\rightarrow$ absorpton, $\leftarrow$ desorption.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 8