

Hydrogen sorption peculiarities in FeTi-type Ti–Fe–V–Mn alloys

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Abstract

The interaction of hydrogen with FeTi-based alloys of the Ti–Fe–V–Mn system was investigated using *P*–*C* isotherms, energy dispersive X-ray analysis (EDXA) and Auger electron spectroscopy (AES). In narrow concentration ranges of both vanadium and manganese, the β - and γ -hydride decomposition pressure values approach each other and the corresponding plateaux transform into one sloping plateau on the desorption isotherm. We call this phenomenon the “pressure smoothing effect”. The alloying of FeTi with vanadium and manganese does not lead to considerable changes in the resistance of the alloys to contamination. The presence of vanadium and especially manganese changes the surface properties and influences the activation mechanism of hydrogen absorption.

1. Introduction

The intermetallic compound FeTi reacts with hydrogen to form the β -monohydride and γ -dihydride phases [1]. Various types of FeTi alloys containing additions of transition metals have been proposed for practical use [2]. The presence of manganese in such alloys increases the rate of the first hydriding and improves the resistance to surface poisoning by impure hydrogen. Some workers have connected this effect with the greater affinity of manganese for oxygen [3].

The effect of alloying FeTi with manganese and vanadium on the hydriding characteristics of this compound has been investigated [4–7]. Additions of vanadium or manganese up to 10 at.% do not change the absorption capacity and lead to a gradual decrease in the decomposition pressure in the two-phase ($\alpha + \beta$) region [5–7]. Formal substitution according to the chemical formula of FeTi, in particular when both titanium and iron are replaced by manganese (up to 10 at.%), leads to a decrease in the decomposition pressure and a dramatic fall in the absorption capacity due to the presence of a second $\text{Ti}(\text{Fe}_{1-x}\text{Mn}_x)_{1.5}$ phase, which does not absorb hydrogen [7].

Recently [4], we have reported that the substitution of vanadium (up to 5 at.%) for iron and titanium gives rise to a phenomenon in which the β - and γ -hydride decomposition pressure values approach each other and the corresponding plateaux transform into one sloping

plateau on the desorption isotherm. We call this phenomenon the “pressure smoothing effect”. In this paper, we report the results of an investigation into the joint influence of manganese and vanadium on the hydriding characteristics of FeTi.

2. Experimental details

The alloys were prepared by melting titanium (99.99%), iron (99.99%), vanadium (99.9%) and manganese (99.9%) in an argon-arc furnace. The apparatus for hydriding and obtaining *P*–*C* isotherms has been described [8, 9]. The hydrogen used was of 99.9999% purity from an LaNi_5 accumulator. The unstable hydride phases were obtained for analysis by quenching samples with compositions corresponding to the dihydride and monohydride from ambient to liquid nitrogen temperature, evacuating the samples to 10^{-2} atm, poisoning the samples with air (oxygen) and heating to room temperature under an air pressure of approximately 5 atm. The hydride phases obtained in this way were rather stable and hardly lost hydrogen in air over a period of 1 month. The X-ray analysis was carried out using DRON-2 and Rigaku X-ray spectrometers with Cu $K\alpha$ radiation. Semi-quantitative energy dispersive X-ray analysis (EDXA) was performed with a KYKY-1000B scanning electron microscope. The precision of element concentration determination is about 5%.

Auger electron spectroscopy (AES) was carried out using a VG ESCA LAB5.

3. Results and discussion

3.1. Characteristics of the initial alloys

The characteristics of the initial alloys are presented in Table 1. The ternary alloys are single-phase samples which is in agreement with the Ti-Fe-Mn phase diagram [10]. The cell parameters increase with increasing manganese content due to the larger metallic radius of manganese compared with that of iron.

The Ti-Fe-V-Mn phase diagram is not known from the literature. In addition to the main δ -FeTi phase, all quaternary alloys also contain a small amount of a second hexagonal C14 phase. For the two-phase alloys the cell parameters remain practically unchanged. According to the X-ray data the amount of the C14 phase increases at higher concentrations of manganese.

3.2. P-C isotherms

3.2.1. Ti-Fe-Mn alloys

On exposure to hydrogen the alloys (2 g) start to absorb hydrogen without any preliminary activation or induction period. However, the reaction is rather slow and full absorption is complete in about 12 h. After this, the hydrogen absorption-desorption equilibrium is reached within 0.5 h. The absorption capacity remains

TABLE 1. Characteristics of the initial alloys investigated in this study

Alloy	Ti (at.%)	Fe (at.%)	Mn (at.%)	V (at.%)	Cell parameters (Å)		Phase
					a	c	
1	49	46	5		2.976		FeTi
2	50	40	10		2.983		FeTi
3	48	40	12		2.990		FeTi
4	50	35	15		2.994		FeTi
5	45.7	44.7	8.4	1.2	2.971		FeTi Traces C14
6	45.7	44.7	7.2	2.4	2.978		FeTi
					4.874	7.914	C14
7	45.7	44.7	4.8	4.8	2.981		FeTi
					4.872	7.917	C14
8	45.7	44.7	1.2	8.4	2.983		FeTi
					4.873	7.915	C14
9	43.6	42.8	9.1	4.5	2.990		FeTi
					4.876	7.918	C14
10	41.7	41.0	13.0	4.3	2.987		FeTi
					4.876	7.915	C14
11	40.0	39.1	16.7	4.2	2.994		FeTi
					4.876	7.920	C14
12	48	37	10	5	2.988		FeTi
					4.878	7.919	C14

practically unchanged for all the alloys. Values of the decomposition pressure decrease with increasing concentration of manganese (Fig. 1). The desorption isotherms for the alloys 2 and 4 (Table 1) are in good agreement with the isotherms for the same alloys obtained previously [5, 7]. For alloys containing up to 15 at.% Mn, we can clearly see in Fig. 1 that the isotherms exhibit only one sloping plateau. This means that, for these alloys, the "smoothing" effect of the β - and γ -hydride decomposition pressures occurs.

3.2.2. Ti-Fe-V-Mn alloys

We wish to determine the compositions of the quaternary alloys which exhibit the same "smoothing" effect. Two directions of search were used: (1) addition of manganese to the alloy having a composition of $Ti_{0.48}Fe_{0.47}V_{0.05}$ while preserving a constant Ti to Fe to V ratio; (2) variation of the ratio between vanadium and manganese while keeping the Ti to Fe ratio unchanged. In Fig. 2 we can see the approximate variants in the quasi-ternary FeTi-V-Mn phase diagram where the alloys employed in this investigation are marked by filled squares.

Alloying the base $Ti_{0.48}Fe_{0.47}V_{0.05}$ sample with the same amount of manganese as vanadium leads to a very good result (Fig. 3). Alloy 7 forms a dihydride phase and the desorption of hydrogen formally proceeds by only one plateau pressure. The form of the isotherms at 323 and 353 K clearly suggests the existence of a monohydride phase with the composition $Ti_{0.457}Fe_{0.447}V_{0.048}Mn_{0.048}H_{0.5}$. An increase in temperature gives the critical point of existence of the $\beta \leftrightarrow \gamma$ transition. At 323 K the isotherm exhibits a considerable

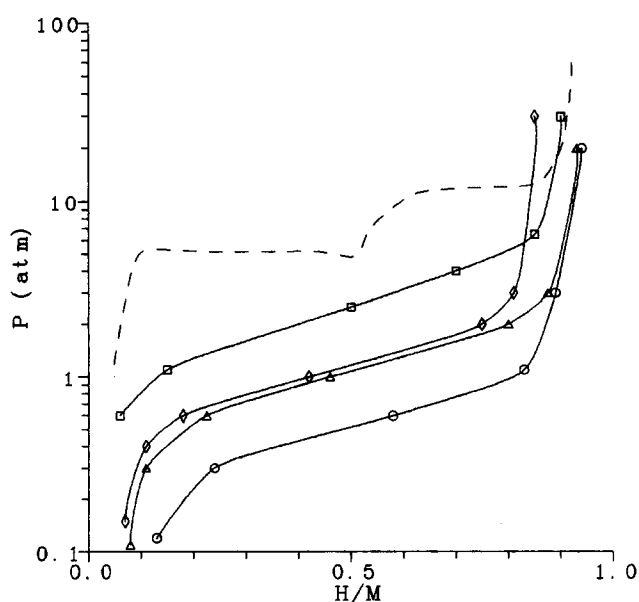


Fig. 1. Desorption isotherms for the alloys 1-4 (specified in Table 1) at 295 K: \square , 1; \triangle , 2; \diamond , 3; \circ , 4; ---, FeTi at 300 K [1].

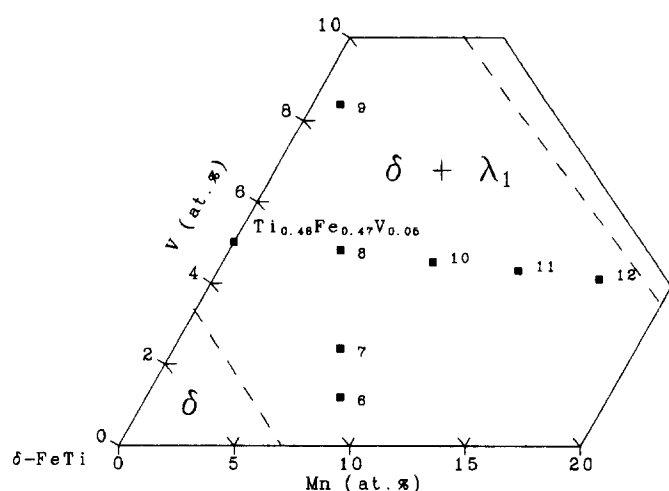


Fig. 2. Portion of the quasi-ternary FeTi-V-Mn phase diagram.

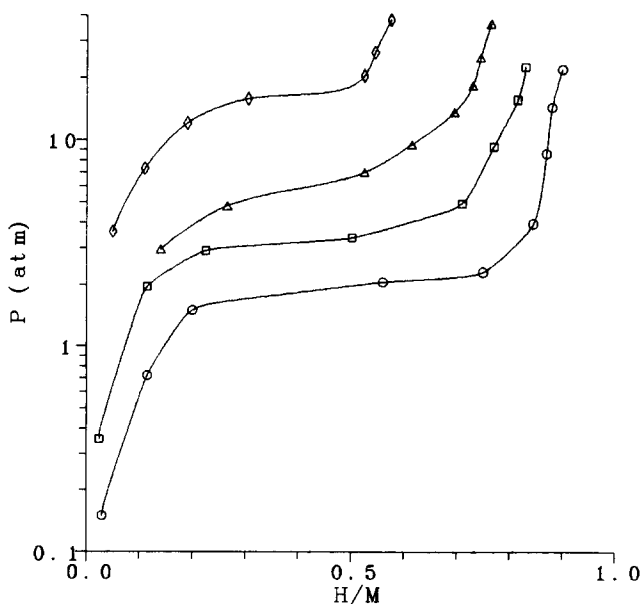


Fig. 3. Desorption isotherms for the $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}\text{-H}_2$ system: \circ , 295 K; \square , 303 K; \triangle , 323 K; \diamond , 353 K.

slope in the range 0.5–1.0 H/M. At 353 K the maximum hydrogen absorption is equal to only 0.6 H/M. This feature is almost the same as in the FeTi-H system [1].

The thermodynamic characteristics of hydrogen interaction with $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}$ were determined using the decomposition pressures of the β -monohydride phase at various temperatures: $\Delta H_{\text{des}} = 28.6 \text{ kJ (mol H}_2\text{)}^{-1}$; $\Delta S_{\text{des}} = 104 \text{ J (mol H}_2\text{)}^{-1} \text{ K}^{-1}$. Additions of vanadium and manganese lead to a decrease in the decomposition pressure and to an increase in reaction enthalpy compared with the FeTi-H system, which agrees with previous results [5–7]. The characteristics of the $\gamma \rightarrow \beta$ transition determined for the composition with H/M=0.65 are $\Delta H_{\text{des}} = 44.9 \text{ kJ (mol H}_2\text{)}^{-1}$ and $\Delta S_{\text{des}} = 159 \text{ J (mol H}_2\text{)}^{-1} \text{ K}^{-1}$. These

values should be considered as tentative because of the considerable slope of the isotherms in the ($\beta + \gamma$) plateau region.

Further addition of manganese, whilst keeping the Ti to Fe to V ratio constant at 1:0.98:0.1 (alloys 9–11), leads to a gradual decrease in the dissociation pressure (Fig. 4) and a dramatic decrease in the absorption capacity due to a decrease in the critical temperature. The amount of residual hydrogen (which cannot be desorbed in the experimental conditions) increases. This is due to the increasing concentration of the second C14 phase which reacts with hydrogen but only desorbs it at elevated temperatures (approximately 450 K).

Substitution of manganese for iron in $\text{Ti}_{0.48}\text{Fe}_{0.47}\text{V}_{0.05}$ (alloy 12, Fig. 5) has little effect on the absorption capacity. However, there is a decrease in the dissociation pressure and the β -hydride phase region becomes more distinct.

If we vary the vanadium and manganese content (but keep it below 10 at.% Mn and/or V) and maintain a constant Ti to Fe ratio (alloys 5–8), we can clearly see from Fig. 5 that the amount of vanadium is especially effective in generating the “smoothing” phenomenon. However, it should be noted that this phenomenon only takes place in a narrow range of vanadium concentration. A vanadium content above 4.8 at.% results in an isotherm with two distinguishable plateaux, while an increase in manganese content leads to the disappearance of the dihydride phase.

3.3. X-Ray analysis of hydride phases

Results of the X-ray analysis of the hydride phases forming in the $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}\text{-H}$ system pro-

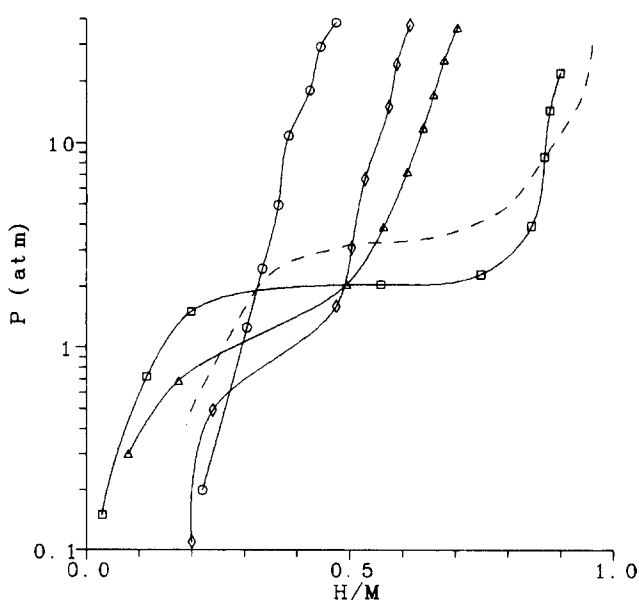


Fig. 4. Desorption isotherms for the alloys 7, 9–11 (specified in Table 1) at 295 K: \square , 7; \triangle , 9; \diamond , 10; \circ , 11; ---, $\text{Ti}_{0.48}\text{Fe}_{0.47}\text{V}_{0.05}$.

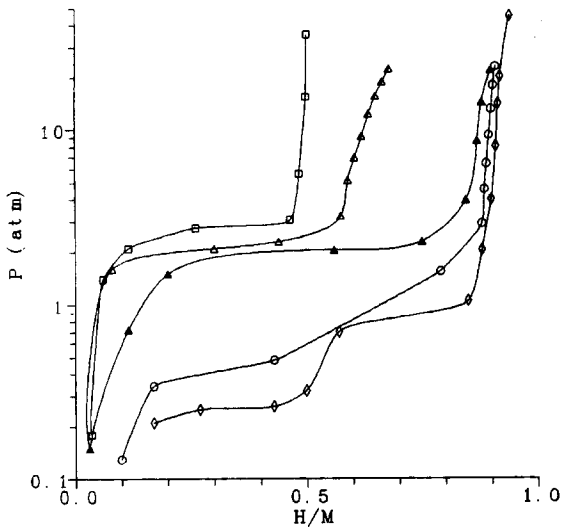


Fig. 5. Desorption isotherms for the alloys 5-8 and 12 (specified in Table 1) at 295 K: \square , 5; \triangle , 6; \blacktriangle , 7; \diamond , 8; \circ , 12.

vide further evidence of the existence of β - and γ -hydrides. $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}\text{H}_{0.95}$ crystallizes in a monoclinic structure with lattice parameters of $a = 4.272 \text{ \AA}$, $b = 2.841 \text{ \AA}$, $c = 4.722 \text{ \AA}$ and $\beta = 97.14^\circ$ which are in good agreement with the values for FeTiH_2 [11]. The X-ray pattern of $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}\text{H}_{0.5}$ includes, in addition to the reflections of the main orthorhombic phase (cell parameters $a = 2.650 \text{ \AA}$, $b = 4.601 \text{ \AA}$, $c = 4.326 \text{ \AA}$), some peaks of the initial phase. The hydride with the composition $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}\text{H}_{0.7}$, which according to the isotherm belongs to the $(13 + \gamma)$ region, is a two-phase sample with cell parameters for the γ phase of $a = 4.730 \text{ \AA}$, $b = 2.839 \text{ \AA}$, $c = 4.726 \text{ \AA}$ and $\beta = 97.17^\circ$ and for the β phase of $a = 2.656 \text{ \AA}$, $b = 4.607 \text{ \AA}$ and $c = 4.342 \text{ \AA}$. For all of these phases there are some additional peaks associated with the presence of the C14 phase. From its cell parameters it can be inferred that this phase also absorbs hydrogen to form an α solution.

It should be noted that it is difficult to obtain the pure monohydride FeTi-type phase using the procedure described in Section 2. It is difficult to determine the exact concentration range of the β phase on a "single plateau" isotherm. The sample may contain traces of the initial phase. Quenching in liquid nitrogen before "oxygen stabilization" takes a finite time and absorption of hydrogen due to the decreasing temperature may take place which leads to the appearance of the γ phase. For this reason, the resulting $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}\text{H}_{0.5}$ sample may be a metastable three-phase system containing traces of the α and γ phases.

3.4. Contamination

The alloy $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}$ is a promising material for hydrogen storage applications. Experiments

were carried out to determine the resistance of this alloy with regard to surface poisoning. The absorption-desorption cycles were performed using technical grade purity hydrogen containing oxygen (2250 ppm) and water vapour (2500 ppm). As can be seen from Fig. 6, after ten cycles the absorption capacity reduces to 0.5 H/M. The isotherm exhibits a considerable slope. However, after reactivation of the sample at 770 K in a vacuum of 10^{-2} mmHg the full capacity can be restored. It is even slightly higher than the capacity in the first run mainly due to the surface increase as a result of cycling. However, after six cycles or more it decreases to the same value of 0.5 H/M.

The addition of a small quantity of LaNi_5 to eliminate oxygen and water vapour does not change the results. Therefore, as observed for $\text{Ti}_{0.48}\text{Fe}_{0.47}\text{V}_{0.05}$ [4], this alloy ($\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}$) has a very low resistance to surface contamination and an affinity for oxygen even higher than that of LaNi_5 .

These results and the previous data [4] show that all the alloys of the FeTi group are not suitable for practical applications in hydrogen accumulators using technical grades of hydrogen. However, they can be used in installations with closed circulation of pure hydrogen, such as thermosorption compressors.

3.5. Energy dispersive X-ray analysis and Auger electron spectroscopy of hydrides

The results of EDXA are shown in Table 2. In the surface layers of the initial sample (approximately 5000 \AA) the composition is slightly different from that of the bulk alloy. These layers are enriched in iron and

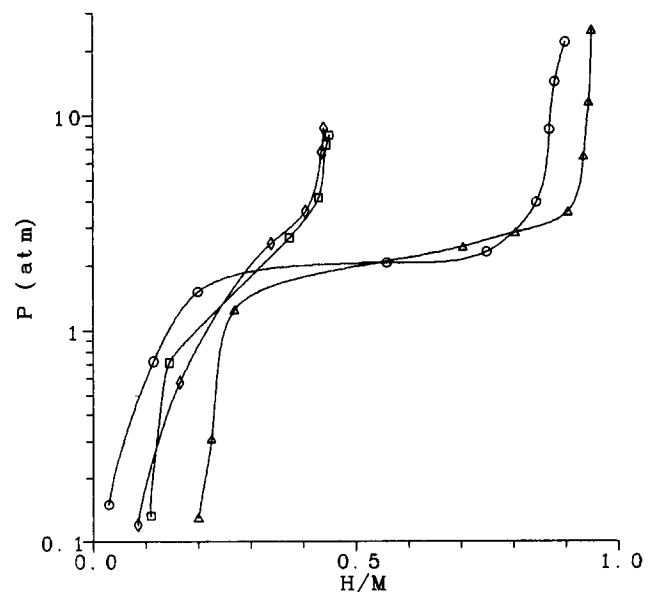


Fig. 6. Effect of cycling at 295 K in technical grade hydrogen on desorption isotherms for $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}$ alloy: \circ , cycle 1; \square , cycle 10; \triangle , cycle 11 (activated at 770 K); \diamond , cycle 16.

TABLE 2. Semi-quantitative EDXA results

Element	Concentration (at.%)				
	Bulk	Initial	Monohydride	($\beta + \gamma$)	Dihydride
Ti	45.7	43.9	43.5	43.8	41.8
Fe	44.7	47.2	46.8	46.7	48.6
V	4.8	4.7	5.8	5.3	5.3
Mn	4.8	4.2	3.9	4.2	4.3

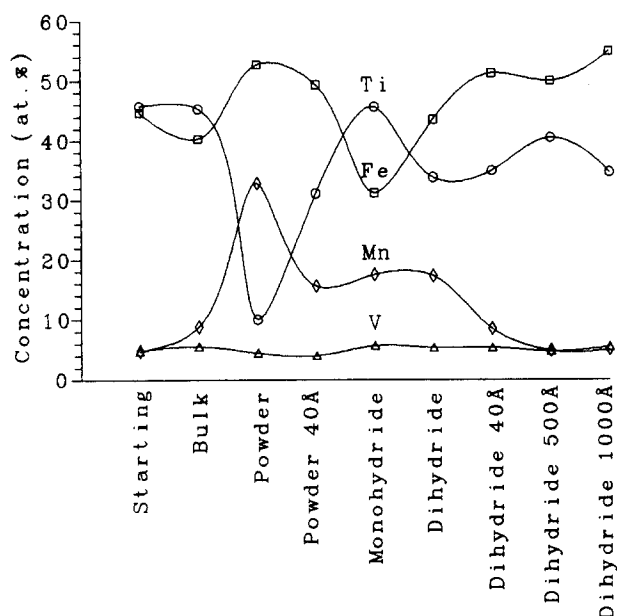


Fig. 7. Change in surface metal concentration for different samples of $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}$ and its hydrides as measured by AES.

have titanium concentrations slightly lower than the average value. On hydriding, these values do not change within the error limits. However, there is a clear increase in vanadium concentration.

This picture changes significantly if we analyse the thin surface layers by AES. From Fig. 7 it is clear that, in the initial bulk alloy, the surface layer is slightly enriched in manganese and the concentration of iron is somewhat below the average value. The concentrations of the other metals remain practically the same. After crushing the initial alloy into fine powder there is a dramatic decrease in the titanium surface concentration and a simultaneous increase in manganese concentration, while as shown in refs. 12 and 13, the upper layers of FeTi are enriched in titanium. This seems to be the main difference in the state of the surface of the alloy compared with FeTi. These surface changes should ease the activation process of the vanadium-manganese-containing alloys.

Argon sputtering of the powder $\text{Ti}_{0.457}\text{Fe}_{0.447}\text{V}_{0.048}\text{Mn}_{0.048}$ sample shows that the segregation does not progress very deeply and even at approximately

40 Å the metal concentrations equal the average bulk values.

Seiler *et al.* [14] have shown that exposure of the pure alloy to oxygen does not change the concentration of metals in the surface layers. Hence we can assume that the quenching procedure employed to prepare the stable hydride phases does not influence the results of the Auger analysis and all the effects are due to the presence of hydrogen in the metallic matrix.

As can be seen from Fig. 7 the absorption of hydrogen does not lead to great changes in the surface composition. The upper layers are enriched in iron and manganese. Argon sputtering shows that only at approximately 500 Å from the surface does the manganese concentration reduce to the bulk value. We can conclude that manganese plays the main antioxidant role in this alloy, which agrees with the results of ref. 3.

4. Conclusions

We have shown that the addition of vanadium and manganese can lead to a significant change in the thermodynamic properties of the hydride phases. For small concentrations of both metals, the "smoothing" effect of β - and γ -hydride decomposition pressure values is observed. This may be of great importance for the practical applications of these alloys.

Although the presence of vanadium and especially manganese changes the surface properties of the alloys, it does not lead to considerable changes in the resistance to surface contamination. Such alloys can only be used in systems with a closed high purity hydrogen circulation.

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