

Effect of Substitution of Iron by Cobalt on Hydrogenation Properties of TiFe

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Abstract: *The influence of the partial substitution of iron by cobalt in TiFe on the hydrogen absorption properties was systematically investigated. The pressure-composition isotherms were determined to establish differences in the thermodynamic properties. When cobalt was added to the classic TiFe compound the hydrogen storage capacity decreased markedly from TiFeH₂ to TiFe_{0.5}Co_{0.5}H_{1.5} and the γ phase was not formed. The addition of cobalt as TiFe_{0.5}Co_{0.5} has beneficial effects on the equilibrium plateaus of the hydrides: the plateaus become flatter and a significant reduction in the pressure hysteresis is observed. There is an α phase (hydrogen insertion in a solid-solution): the corresponding first part of the isotherms obeys to the Siwertz law ($n_H = P^{1/2}$). The values of ΔH , ΔS and hysteresis factor were obtained from plots of $\ln P_e$ versus $\frac{1}{T}$ using the Van't Hoff relationship.*

Keywords: hydride, storage capacity, hydrogen, absorption, isotherm, hysteresis

1. Introduction

Since it was discovered at Brookhaven Laboratory by Reilly [1] TiFe alloy and its derivative compounds TiFe_{1-x}M_x have been studied. Indeed and whatever their activation is difficult and highly dependent on the stoichiometry, these materials exhibit both high storage capacity thermodynamic and kinetic features interesting and low cost prices. Physical-chemical studies undertaken on these systems are summarized in this bibliographical chapter.

TiFeCo is one of the most stable compounds of the diagram (Ti,Fe) published by C.Carter [2] Another study [3], [4] was interested in the phase diagram of the TiFe-H₂ system and found the existence of three phases (α, β, γ) closing each a certain amount of hydrogen. [5], [6] determined experimentally by calorimetric measures the heat of formation and decomposition of hydride TiFeH_x. The other non-stoichiometric compounds TiFe can form hydrides as FeTi_{1.5} which from [7], [8] shows an isothermal having a horizontal level corresponding to a pressure of 5atm and an irreversible portion of hydrogen equal to 0, 2H / mol. Suzuki et al. [9] found that the addition of small amounts of elements or oxides of the rare earth to the FeTi_{1+x} compound improves markedly its hydrogenation properties

The partial or total substitution of the iron by other elements of transition was the subject of several studies [10], [11], [12], [13]. Indeed TiFe_{1-x}M_x compounds (M = Cr, Mn, Co, Ni, with x = 0.5 to 1) show that the two phases (α, β) hydride are widely affected by the substitution which lowers the stability of these hydrides in the direction of (Mn to Ni) the same is observed for the hysteresis in the P-C-T diagrams.

The studies made by the techniques of X-ray diffraction, neutron diffraction or Mössbauer are intended to define the volume of the unit cell of the hydride and the position of the hydrogen into the alloy. A profound crystallographic study [14] indicates that crystallized TiCo absorbs 35% of H₂ more than amorphous TiCo this result shows the importance of the crystalline structure during the absorption of

hydrogen. Among the alloys have an ordered structure appears TiFe (F.C.C type CsCl) with a lattice parameter a = 2,980Å. On the other hand [15] structure TiCo_{1-x}A_x compounds with (A = V, Cr, Mn, Fe, Ni, Cu, La, and x = 0.5 to 0,05) remains similar cubic structure to the TiCo base alloy. However the loading of the alloy by the hydrogen causes an increase (8 à 10%) in the unit cell volume.

Comparing the electronic and structural data [16], [17], [18], [19] of TiCoH_x and TiFeH_x shows similar results for the compositions x = 1 (phase β_1) and x = 1.5 (phase β_2) which had an orthorhombic structure while the monoclinic structure corresponding to the composition x = 2 (phase γ) for TiFeH_x does not exist for TiCoH_x which is limited to the maximum TiCoH_{1.5} composition. to give an explanation to the fixing of hydrogen in the cell of TiFe [20], [21]

a neutron diffraction study suggests that the hydrogen atom preferably occupies octahedral sites formed by 4Ti and 2Fe for [22], [23], [24] the location of the hydrogen in one of the sites (Terta or octa) is still poorly known. In order to simplify [10] assumes that the sites are similar and that the substitution of iron in the TiFe_xM_{1-x} alloy leads to three types of sites characterized by the following arrangement: 4Ti+2Fe ; 4Ti+Fe +M ; 4Ti+2M. NMR measurements [25], [26] made on non hydriding TiFe_xCo_{1-x} compounds assumes that the number of each site may be given by the following formulas: $N_1 = Nx^2$; $N_2 = 2Nx(1-x)$; $N_3 = N(1-x)^2$ where x is the fraction of the residual iron in the TiFe_xM_{1-x}. Generally hydriding intermetallic compounds led to an expansion of their mesh and the stability of the hydride increases with the size sites [27]. The study of magnetism in TiFe_{1-x}Co_x-H₂ systems was the subject of several studies [28], [29], [30], [31] it observed lower Curie temperatures (Tc) and small moments magnetic about (0,15 μ B) and the substitution of the iron by cobalt up to 65% does not lead to change in the magnetic properties of the starting sample TiFe. We also detected a high paramagnetic film on the surface of TiFeH_{1,07} [32], [33], [34]. The adsorption of hydrogen on the metal surface appears one of the most important steps in the kinetics of hydriding alloys. However

this surface often presents inhomogeneities due to the formation of very thin oxide layers during spraying samples [35],[36]. The presence of oxygen, oxides or hydroxides induces segregation of the sample surfaces and inhibits or slowed generally the hydrogenation rate which requires a prior activation [37],[38] under a high vacuum and a temperature of 350°C. The hydrogen solution in TiFe and $\text{Ti}_7\text{Fe}_3\text{O}_2$ [39],[40],[41] results from a differential expansion which causes cracking of the oxide.

2. Experimental Details

The compound $\text{TiFe}_{0.5}\text{Co}_{0.5}$ is prepared by direct arc melting under argon atmosphere of the pure components (Ti : 99,99% , Fe : 99,99% , Co : 99,99%) in stoichiometric proportions. The samples are made homogeneous by several remelting and are annealed. The compound is checked by microprobe analysis. Micrographics show that it is single phased. The hydrogen used is the (U) quality of Air Liquid and is made free of residual water and oxygen traces by passing it through cartridge of molecular Sieverts. All the thermodynamic and kinetic experiments are carried out by thermogravimetry in a high pressure microbalance with a limiting sensitivity of 2 μg . The pressure range is from vacuum 2.10^{-4} Pa to pressures up to 10 MPa. Temperatures vary from ambient up to 600°C. Thermogravimetry allows step by step P-C-T diagram determination by equilibrium points i.e. : the system is maintained under stable pressure and temperature conditions until there is no longer a mass change. The isotherms are explored both in formation and decomposition to determine the hysteresis. Kinetic studies are also carried out in the same device on sample masses of 50mg. One grain is laid in a silica sample holder to obtain, after activation, a powder bed of large surface and a thickness of about 0.1mm to minimize heat gradients

3. Results and Discussion

3.1 First hydriding kinetic

The compound $\text{TiFe}_{0.5}\text{Co}_{0.5}$ absorbs hydrogen at 25°C under a pressure of 4 MPa, the first absorption kinetic begins slowly after an induction period of 5 hours and results in the final composition hydride $\text{TiFe}_{0.5}\text{Co}_{0.5}\text{H}_{1.5}$ after 48 hours of reaction (Fig.1)

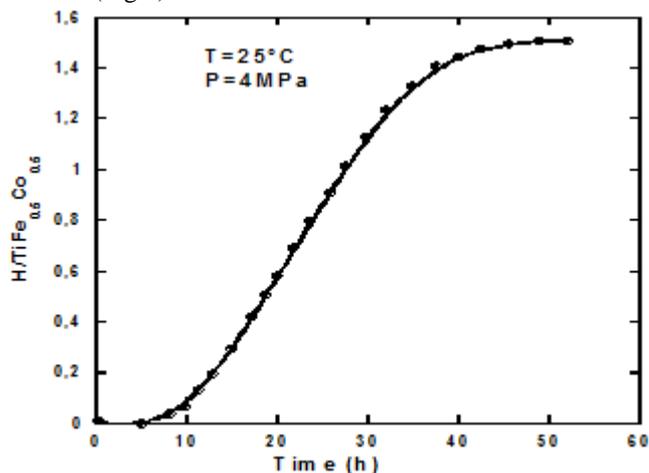


Figure 1: kinetic of first hydrogen absorption by $\text{TiFe}_{0.5}\text{Co}_{0.5}$

3.2 Influence of the preliminary treatment

This treatment consists of heating the sample under vacuum (10^{-5} Pa at 200°C) for one hour followed by cooling to 25°C the figure.2 shows the effect of such treatment on behavior of the alloy with hydrogen. It is observed the disappearance of the latency time and acceleration in the reaction rate which reaches the level of saturation after only one hour. For [35],[38],[40] the preliminary treatment is a process of absorption of humidity and gases adsorbed on the surface of the sample

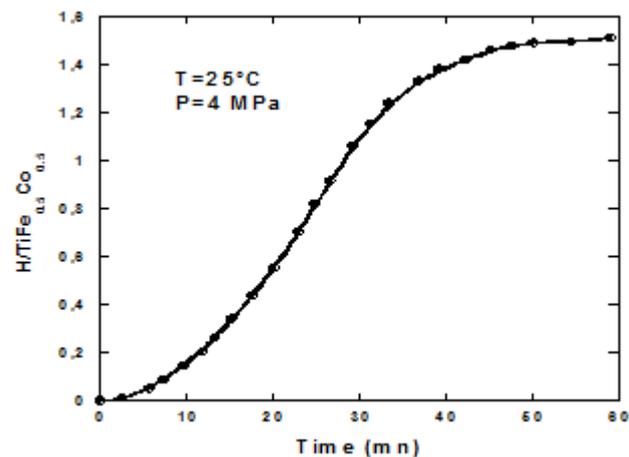


Figure 2: influence of preliminary treatment on the kinetic of first absorption

3.3. Sample Activation

The sample is called activated when after several series of formation-decomposition in the same conditions (4MPa, 25°C) curves overlap. The result is activation from the second cycle (Fig.3) in this graph we see that there is superposition of kinetic curves. These results are in good agreement with those found in the literature [9]

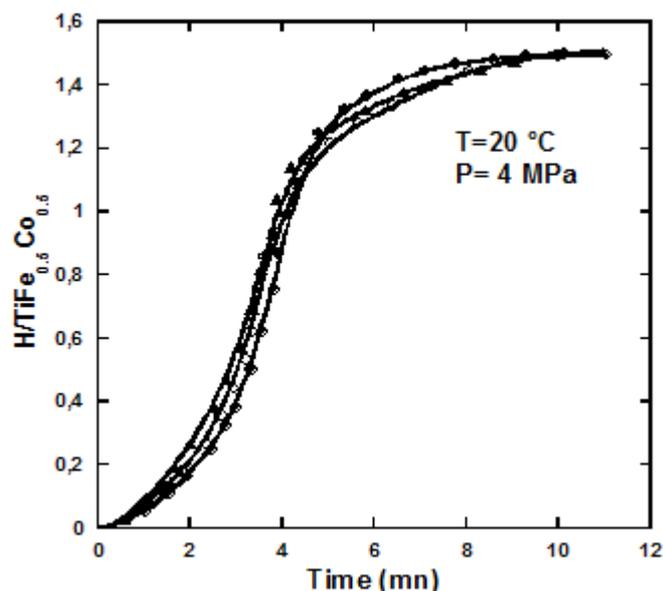


Figure 3: kinetics of the second (●), fifth (○) and tenth (▲) hydrogen absorption by $\text{TiFe}_{0.5}\text{Co}_{0.5}$ (sample activation)

3.4 Thermodynamic Study

In the preliminary to the kinetic study it is firstly necessary to specify the hydride stability areas. This thermodynamic character study is to determine for a given temperature and for different values of the pressure, the nature and composition of phases present. The domain of existence of these phases is formed depending on the temperature (T) in a diagram (P, C) by isotherms family. The almost of alloys shown in a domain which depends on the system a miscibility gap between the α and β phases which results in a level or pseudo-level in where the two phases coexist in the graph (P-C-T), further the presence of hysteresis between the formation and decomposition shows their imperfect reversibility. Our isothermal for $TiFe_{0.5}Co_{0.5}$ compound have been traced between 80 and 120°C from the hydrogen storage composition limit; notice that some compositions under low pressures necessities some days to get the equilibrium plateau. (Fig.4) groups isothermal absorption-desorption of $TiFe_{0.5}Co_{0.5}-H_2$ system, these results will allow us to see that the system exhibits hysteresis between the formation and decomposition of the hydride and the absorption capacity decreases with temperature.

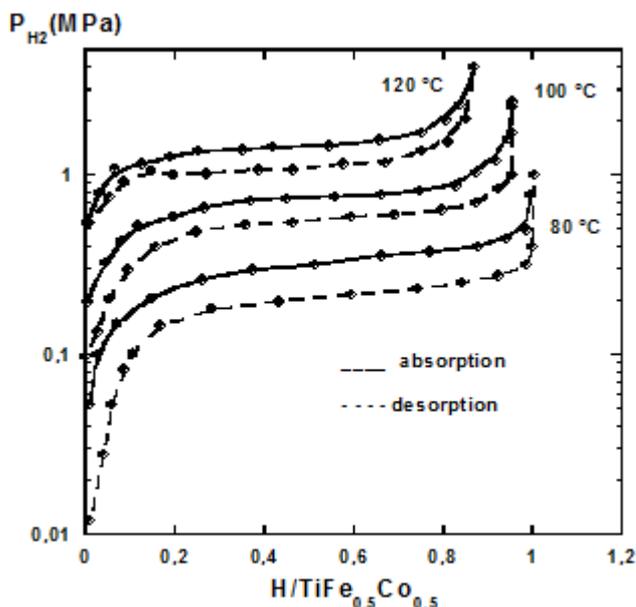


Figure 4: Pression-Composition-Temperature diagrams of $TiFe_{0.5}Co_{0.5}/H_2$ system

Knowledge of absorption and desorption equilibrium pressures gives access to the hysteresis factor $\frac{1}{2}RTLn\frac{P_{e(abs)}}{P_{e(des)}}$ existing between isothermal formation-decomposition and values of ΔH and ΔS using the Van't Hoff law (Fig.5). All the obtained thermodynamic results are grouped in the Table below

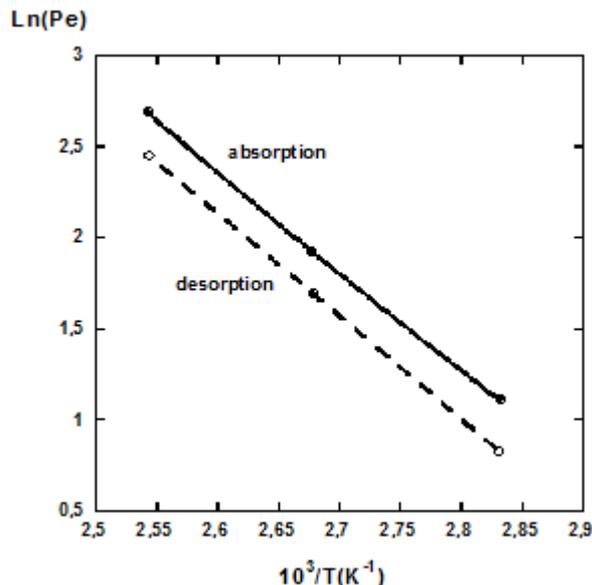


Figure 5: $Ln P_e$ variation in the depending on $1/T$ (Van't Hoff law)

Thermodynamic values for the $TiFe_{0.5}Co_{0.5}-H_2$ system

T°C	80	100	120
Capacity (H/formula)	1	0,95	0,86
$P_{e(abs)}$ MPa	0,30	0,67	1,50
$P_{e(des)}$ MPa	0,22	0,51	1,25
Hyst.factor (J/mol)	455,1	434	306,2
$\Delta H_{(abs)}$ (KJ/mol)	-45,3	-45,3	-45,3
$\Delta H_{(des)}$ (KJ/mol)	49,1	49,1	49,1
$\Delta S_{(abs)}$ (J/mol.K)	-151,2	-151,2	-151,2
$\Delta S_{(des)}$ (J/mol.K)	126	126	126

During this thermodynamic investigation we also identified for much lower pressures than the equilibrium pressure that n_H amount absorbed varies linearly with $P^{1/2}$ (Fig. 6) such a law is called law of Sievert [42] which reflects the existence of an α phase corresponding to the dissolution of a small amount of hydrogen into the $TiFe_{0.5}Co_{0.5}$ alloy

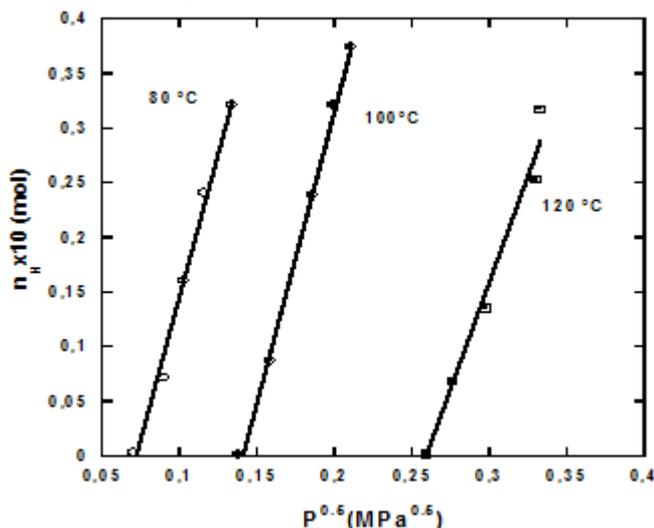


Figure 6 : verification of the Sievert law for $P \leq P_e$

4. Conclusion

Our study on the $TiFe_{0.5}Co_{0.5}-H_2$ system has allowed us to show all of the following properties: The sample activation

is easy. The hydride formed is $\text{TiFe}_{0.5}\text{Co}_{0.5}\text{H}_{1.5}$ which has a thermodynamic stability (0.22MPa at 80°C) lower than that of TiCo (0.1MPa at 130°C) and greater than that of TiFe (0.7MPa at 40°C). The storage capacity decrease with increasing temperature. P-C-T diagrams present an hysteresis between formation and composition and their ascending part suggests the existence of an α phase (solid solution) in the diagram. The absorption-desorption cycles were repeated several times on the alloy but no change observed on the storage capacity. All these characteristics makes $\text{TiFe}_{0.5}\text{Co}_{0.5}$ one of the potential candidates for an eventual hydrogen energy storage.

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