

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 $Ti_7Fe_3O_2$ [39],[40],[41] results from a differential expansion which causes cracking of the oxide.

2. Experimental Details

The compound $TiFe_{0.5}Co_{0.5}$ 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 μ g. The pressure range is from vacuum 2.10⁻⁴ Pa to pressures up 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 $TiFe_{0.5}Co_{0.5}$ 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 $TiFe_{0.5}Co_{0.5}H_{1.5}$ after 48 hours of reaction (Fig.1)

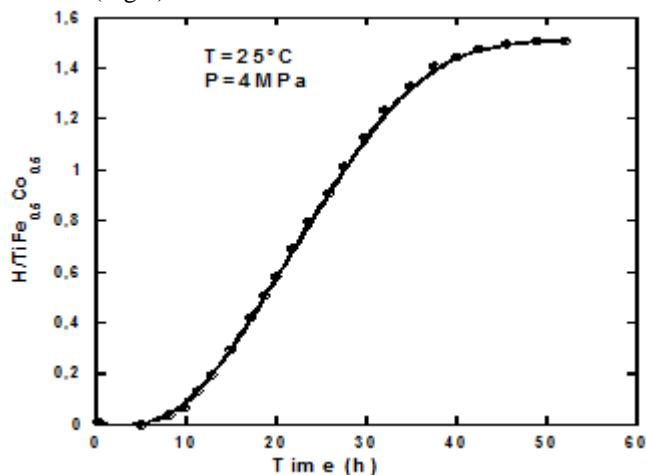


Figure 1: kinetic of first hydrogen absorption by $TiFe_{0.5}Co_{0.5}$

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

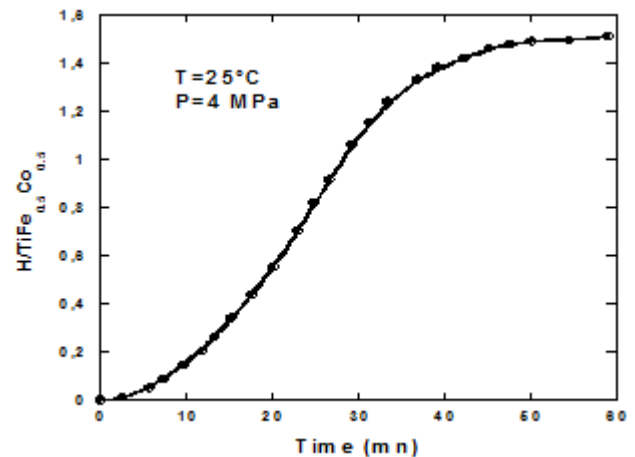


Figure 2: influence of preliminary treatment on the kinetic of first absorption

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]

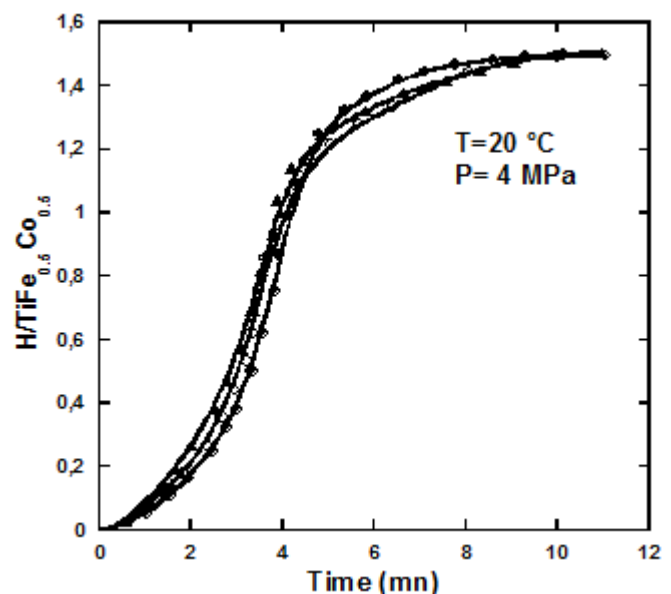


Figure 3: kinetics of the second (●), fifth (○) and tenth (▲) hydrogen absorption by $TiFe_{0.5}Co_{0.5}$ (sample activation)

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.

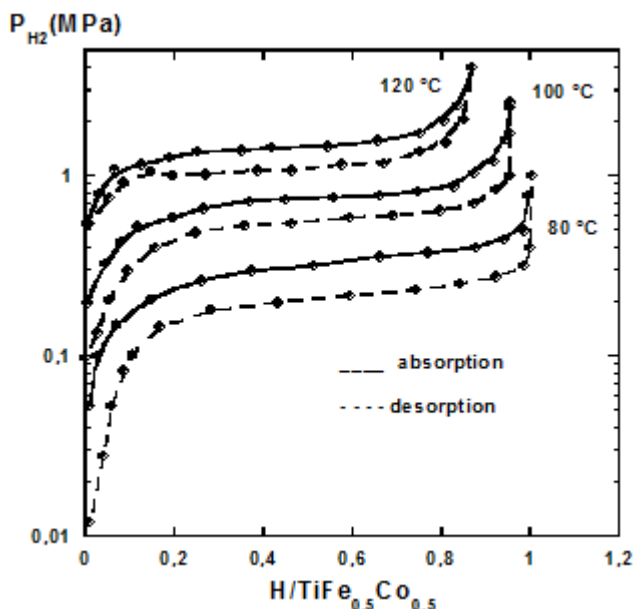


Figure 4: Pression-Composition-Temperature diagrams of $TiFe_{0.5}Co_{0.5}/H_2$ system

Knowledge of absorption and desorption equilibrium pressures gives access to the hysteresis factor $\frac{1}{2}RTLn\frac{Pe(abs)}{Pe(des)}$ 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

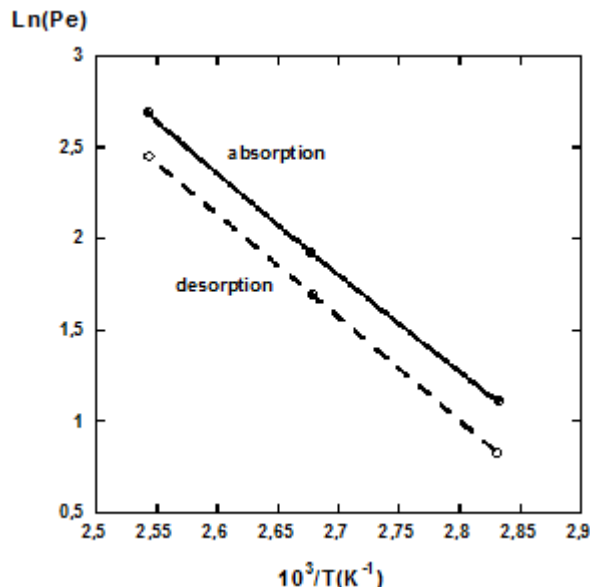


Figure 5: $Ln P_e$ variation in the depending on $1/T$ (Van't Hoff law)

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

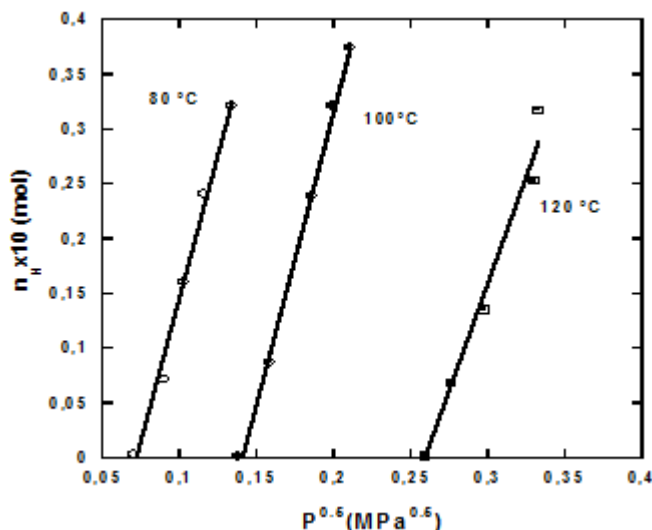


Figure 6 : verification of the Sievert law for $P \leq P_e$

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.

References

- [1] J.J.REILLY , R.H.WISWALL, J.B.N.L, Inorg. Chem., 13(1974) 28
- [2] .G.C.CARTER, L.H.BENNET , Metallic Shifts in MNR Pergamon Press, New york and Oxford (1977) , Corp. Auth : National Bureau of Standard Critical compilation (Book)
- [3] R.C.BOWMAN JR, G.C.CARTER, MNR Studies of hydrogen relaxation and diffusion in TiFeX Symposium on hydrides for energy storage, Geillo, Norway, Ang (1977)
- [4] P.MIET, Advances in Hyd. Product, Storage and Distribution, 2014, Pages 368-409
- [5] H.WENZEL, E.LEBSANFT, J. Phy. F. Met. Phys., 10(1980) 2147-56
- [6] S.-M LEE, T.-P PERNG, Journal of Alloys and Compounds, Volume 291, Issues 1–2, 27 September 1999, Pages 254-261
- [7] P.RAJ, J. Less. Common Met., 130(1987)139-45
- [8] A.P.GUEGAN, M. LATROCH, Journal of Alloys and Compounds, Volume 509, Issue 18, 5 May 2011, Pages 5562-5566
- [9] J.SUZUKI, M.ABE, J. Less. Common. Met., 131(1987)301-309
- [10] BIDERMAN, HADARI, J.Appl.Pys.1(1981) 52
- [11] H. MIYAMURA, M. TAKADA, S. KIKURCHI, Journal of Alloys and Compounds, Volumes 404–406, 8 December 2005, Pages 675-678
- [12] RYUTA WAKABAYASHI, NAOHITO YASUDA, SINO SASAKI, Journal of Alloys and Compounds, Volume 484, Issues 1–2, 18 September 2009, Pages 682-688
- [13] TSUTOMU , KOHEI MAKI, YOSHINORI SASAKI, Journal of Power Sources, Volume 125, Issue 1, 2 January 2004, Pages 52-61
- [14] A.MAELAND,L.E.TANNER,G.G.LIBOWITZ, J. Less .Common Met.,74(1980)279-85
- [15] Y.OUZUMI,H.SUZUKI, A.KATO, J. less. Common Met.74(1980)271-77
- [16] J.S.CANTRELL,R.C.BOWMAN., J. less. Common Met.130(1980)69-78
- [17] NARUKI ENDO, HIROYUKI SAITOH, AKIHIKO MACHIDA, International Journal of Hydrogen Energy, Volume 38, Issue 16, 30 May 2013, Pages 6726-6729
- [18] V.ZADOROZHNYI, S.KLYAMKIN, M. ZADOROZHNYI, International Journal of Hydrogen Energy, Volume 37, Issue 22, November 2012, Pages 17131-17136
- [19] M. ABE, T. KUJI, Journal of Alloys and Compounds, Volumes 446–447, 31 October 2007, Pages 200-203
- [20] P.THOMPSON,JJ.REILLY, F.REIDENGER., J.Phys.F9(1979)L61
- [21] BORISLAV ABRASHEV, TONYSPASSOV, STOYAN BLIZNADOV, International Journal of Hydrogen Energy, Volume 35, Issue 12, June 2010, Pages 6332-6337
- [22] J.SCHEFER, F.PISCHER, W.HALG, Mat. Res. Bull., 13(1978)931
- [23] A.V.BAKULIN, S.S.KULKOV, S.E.KULKOVA, International Journal of hydrogen Energy, Volume 39, Issue 23, 4 August 2014, Pages 12213-12220
- [24] KAZUHIRO, ISHIKAWA, SHOGO WATANABE, Journal of Alloys and Compounds, Volumes 566,25 July 2013 pages 68-72
- [25] L.J SWARTZENDRUBER, L.H.BENNETT.,J.Appl.Phys.39(1968)931
- [26] ŻYWCZAK, Ł. GONDEK, H.FIGIEL, J.ŻUKOWSKI, J. CZUB,TAKASAKI, Journal of Alloys and Compounds, Volumes 509,Issue, 9,3 March 2011 pages 3952-3957
- [27] O.ONO, K.NOMURA,IREDA., J. less. Common Met.72(1980)159-65
- [28] L.H.BENNET) L.J SWARTZENDRUBER., Phys.Res.165(1968)500-6
- [29] A.BLASUS,U.GON SER.,J.Appl.Phys.22(1980)301-12
- [30] MEMPELMAN,OHLENDORF,WIKE.,Proc.Int.Symp. on hydridesfor energy storage, Geilo Norway(London, Pergamon, 1977)
- [31] G. LEE, J.S. KIM, Y.M. KOO, S.E. KULKOVA International Journal of Hydrogen energy, Volume 27, issue 4, April 2002,pages 103-412
- [32] HILSCHER ,GRATZE. , Phys. Status Solid.48(1978)473-80
- [33] J.S. KIM, S.Y. Oh, G. LEE, Y.M. KOO, S.E.KULKOVA, International Journal of Hydrogen Energy, Volume 29, Issue 1, January 2004, Pages 87-92
- [34] GÜNTER WIESENGER, GERFRIED HILSCHER, Handbook of Magnetic Materials, Volume 17, 2007, Pages 293-456
- [35] L.SCHLAPBACH, A.SEILER,H.C.SIEGMAN., J. Hydrogen Energy 4(1979)21-28
- [36] MOEGAMAT WAFEEQ DAVIDS, MYKHAYLO LOTOTSKYY, International Journal of Hydrogen Energy, Volume 37, Issue 23, December 2012, Pages 18155-18162
- [37] P.GUINET, Centre d'étude de Grenoble, Laboratoire ASP Grenoble, France
- [38] MOEGAMAT WAFEEQ DAVIDS, MYKHAYLO LOTOTSKYY, International Journal of Hydrogen Energy, Volume 36, Issue 16, August 2011, Pages 9743-9750
- [39] MATSUMOTO, AMANO., SC.Met., 15(1981)879
- [40] XINHUA WANG, RUGAN CHEN, CHANGPIN CHEN, QIDONG WANG, Journal of Alloys and Compounds, Volume 425, Issues 1–2, 30 November 2006, Pages 291-295
- [41] M. WILLIAMS, M.V. LOTOTSKY M.W. DAVIDS, V. LINKOV, Journal of Alloys and Compounds,

Volume 509, Supplement 2, September 2011, Pages
S770-S774

[42] A. SIEVERTS, Z. Phys. Chem., 88(1914) 451

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