Application of Theoretical Models to the Kinetic Study of the $TiFe_{0,5}Co_{0,5}$ — H_2 System

M. Boulghallat[1], A. Jouaiti, L. Lâallam[2]

Laboratoire de développement durable, Equipe de Corrosion et Traitement des Matériaux, FSTBM, BP523, Beni Mellal (Maroc)

Abstract: *The reaction of hydrogen with metals to form hydrides has numerous potential energy storage and management applications. But initially it is first necessary to determine conditions of hydrogen sorption kinetics. In this paper the hydriding kinetics of $TiFe_{0,5}Co_{0,5}$ are studied. Experiments were carried out in thermo gravimetric microbalance with a high sensibility (2.10^{-6} g) on a series of isothermal and isobaric measurement. The kinetics models, namely Johnson–Mehl–Avrami (JMA) model and Jander diffusion model (JDM) are used to explain the obtained results. In the first model, the order of the reaction is assumed as unit and in the second model, the rate constant is calculated by estimating the order by fitting the reaction kinetics data with a reaction kinetics equation. The activation energy and pre-exponential constants of the above-mentioned alloy are estimated by constructing the Arrhenius plot. The absorption mechanism of hydrogen and rate-controlling step of the reaction are estimated for the hydride investigated.*

Keywords: Hydriding, kinetics, Modeling, Activation energy, mechanism

1. Introduction

Among AB intermetallics, FeTi system was studied [1] various times due to its moderate kinetics with relatively high equilibrium hydrogen pressure (4.5atm) at room temperature. However, low storage capacity (1.8 to 1.9wt%) and O_2, H_2O, CO poisoning problems could not be resolved fully in order to use in practical applications. FeTi has CsCl-type structure which corresponds to Pm.3m space group with a lattice parameter of 2.9789Å. Reilly and Wiswall [2] observed that FeTi reacts readily to form FeTiH1 (α phase) and FeTiH2 (γ phase) according to reactions: 2.13FeTiH0.1(α) + H2 → 2.13FeTiH1.04(β) followed by 2.20FeTiH1.04(β) + H2 → 2.20FeTiH1.9(γ). The effect of partial substitution of iron by cobalt on the hydrogenation properties of the classic TiFe have been recently studied [3] it was found that when cobalt was added to the alloy the hydrogen storage capacity decreased markedly from $TiFeH_2$ 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 partie of the isotherms obeys to the Siervert law ($n_H = P^{1/2}$). In the same way some TiFe-based alloys have been developed [4] according to the stoichiometry Ti1−xAxFe1−yBy (A ≡ Zr; B ≡ Mn, V). The hydrogen solubility properties have been investigated to develop dynamic hydrides of Ti-based alloys for hydrogen storage applications. The Ti1.9CrVFe0.1, Ti1.9CrVCo0.1 and Ti1.9CrVNi0.1 alloys are found [5] to absorb maximum 3.80, 3.68 and 3.91 wt.% of hydrogen respectively; whereas, Ti1.8CrVCo0.2 and Ti1.8CrVNi0.2 alloys show 3.52 and 3.67 wt.% of hydrogen at room temperature. All the alloys show fast hydrogen absorption kinetics at the room temperature. From differential scanning calorimetric measurements, it has been found that Fe, Ni and Co substitution in place of Ti decreased the hydrogen desorption temperature drastically compared to the parent alloy. For [6] the insertion of hydrogen into the structure causes an increased electron density in the electronic orbital's of Fe which were oriented towards hydrogen atoms,

he has also identified a new hydride which is less stable than the experimentally observed ones, having four hydrogen atoms per chemical formula.

TiFe-based hydrogen storage materials are highly sensitive towards gas impurities which induce a significant deterioration of the hydrogen absorption performances. An efficient solution to this problem is in modification of the material surface by the deposition of metals (including Palladium) capable of catalyzing the dissociative chemisorptions of hydrogen molecules. In their work [7],[8],[9],[10] the surface modification of TiFe alloy was performed using a metal-organic chemical vapour deposition technique (MOCVD), by the thermal decomposition of palladium (II) acetyl acetonate (Pd[acac]2) mixed with the powder of the parent alloy. Such a treatment was shown to result in the formation of coatings comprised of palladium nanoparticles, which subsequently facilitate the hydrogenation of the material even after its exposure to air, which otherwise prove detrimental. However, the hydrogenation performances were found to be quite sensitive to MOCVD conditions that, most probably, originates from side processes in the interaction of gaseous products of Pd [acac]2 decomposition with TiFe. The sorption kinetics of the hydride-forming alloy $TiFe_{0.8}Ni_{0.2}$ were investigated [11] Overall isothermal reaction rate measurements were interpreted by assuming a first-order rate law. The decomposition rates of $TiFe_{0.8}Ni_{0.2}H$ after cycling were found to be lower than those obtained for non-cycled (activated only) alloy The studies [12] reported on the materials alloy promising results, such as improved kinetics and lower decomposition temperatures. However, in spite of this large number of kinetic studies, it is still much effort to be done to better understand the kinetic mechanisms of hydrogen diffusion in metallic alloys

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
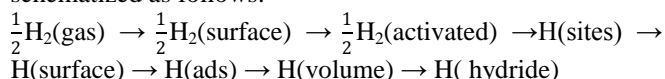
Paper ID: SUB1520

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 Sievert's. All the thermodynamic and kinetic experiments are carried out by Thermogravimetry in a high pressure microbalance with a limiting sensitivity of 2µg. 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 The Basic Steps of the Hydrogen Diffusion

the sequence of the elementary steps which occur during the absorption of hydrogen by the metal compounds can be schematized as follows:
$\frac{1}{2}H_2(gas) \rightarrow \frac{1}{2}H_2(surface) \rightarrow \frac{1}{2}H_2(activated) \rightarrow H(sites) \rightarrow H(surface) \rightarrow H(ads) \rightarrow H(volume) \rightarrow H(hydride)$

1-mass transport: it is possible that this step is the slowest on condition that the particles to be smaller and/or porous and that the rate of the reaction is fast[13]

2- chemisorptions of the hydrogen molecule: the number of molecules of the gaseous phase which shock the unit surface per second is equal to $P/(2\pi mRTK)^{1/2}$ in wich m represents the mass of a molecule, P the pressure in the pore neighborhood and K the Boltzman constant. The probability of adhesion is defined as the ratio of the number of molecules that stay on the surface on the total number of collision the adhesion rate U (expressed as adsorbed molecules per second per cm^2) can be expressed as follows $U=S.P/(2\pi mK)^{1/2}$. For simple adsorption activated $S= \sigma.f(\theta)\exp(- Ea/RT)$ with $f(\theta)$ is a function of the surface covering rate and represents the probability that a collision occurs on a valid site, the rate equation becomes $U= \sigma.P(2\pi mK)^{1/2} f(\theta)\exp(- Ea/RT)$

3-dissociation of the hydrogen molecule : if this step is regulative and the previous step is in equilibrium in this case the rate of collection at the pressure P_o is given by the adsorption law Langmir : $\theta = K_1P_o /K_2+K_1P_o$; K_1 and K_2 are the constant rate in both directions

4-diffusion of hydrogen sites to the metal surface : the diffusion of hydrogen on the surface is more complicated when must be considered the remaining Jx fux previous

steps and hydrogen diffusion flux to the surface in the steady state[14]:

$\partial Jx/\partial x + Jx = 0$

5-transformation of the chemisorbed state to absorbed state: H(chemisorbed) → H(absorbed) in this step the flux is given by: $J= K_1C_o -K_2C_\beta$ in wich C_β is the concentration of hydrogen in the hydride phase, at the equilibrium pressure $C_o = C_{eq}$

6-diffusion through the hydride phase : step in which we assume a uniform attack leading to almost instantaneous formation of a protective layer [15] the progress of the reaction result of the synchronization of the following three phenomena:
- interfacial reaction external at the interface gas-solid B
- internal interfacial reaction at the interface solid A-solid B
- the diffusion between the two interfaces of the thickness of the product B

7-transformation phase : in this case the absorption and diffusion rates are larger than that corresponding to the precipitation of the new α phase, of which the composition can only be considered a function of the initial pressure imposed. The equation for the rate of the regulating step of the precipitation can be written as follows:
$V= K(P_{H2}- P_{H2}eq)$ with $(H)_{dissolved} = AP_{H2}$

3.2. Some numerical data generally used in the equations of solid reactions

A large number of reactions in the solid state may be represented by type equations $F(\alpha) = Kt$, where a is the fraction of the material which has reacted at time t. These equations can also be expressed in the form $F(\alpha) = A (t/ t_{0.5})$ where $t_{0.5}$ is the half reaction time and A is a constant which depends on $F(\alpha)$. This function $F(\alpha)$ depends also on the reaction mechanism, the size and form of the reacting particles. However in the kinetic study of solid reactions significant simplification occurs for some parameters (size, shape) of the reactant solide. Then we find classical equations for the evolution of the heterogeneous reaction for some typical cases.

3.2.1.Reactions controlled by diffusion which starts at the outside radius r of particles
This type of reactions is characterized by the Valensi [17] equation:

$$D_4(\propto) = \left(1 - \frac{2}{3}\propto\right) - (1-\propto)^{2/3} = \left(\frac{K}{r^2}\right)t \quad \boxed{1}$$

for comparing this theoretical equation to the experimental data, it is more convenient to employ the reduced time $t/t_{0.5}$, thus $D_4(\alpha)$ equation is reduced to

$$D_4(0.5) = 0.0367 = \left(\frac{K}{r^2}\right)t_{0.5} \quad \boxed{2}$$

by combining $\boxed{1}$ and $\boxed{2}$ we obtained

$$D_4(\propto) = 0.0367\left(\frac{t}{t_{0.5}}\right) \quad \boxed{3}$$

Paper ID: SUB1520

464

From the equation ③ a simple curve can be traced and will be compared directly with experimental data to all pressures and all temperatures. The dependence α variables (T, P, ...etc) is contained in $t_{0.5}$, the constant (K /r^2) is determined from experimental data or from of equation ② or simply from the equation ① by tracing D_4 (α) versus time. The slope of the droite obtained is (K /r^2)

3.2.2. Reactions controlled by diffusion

For a one-dimensional diffusion with a constant diffusion coefficient, the reactions are governed by the parabolic law equation:

$$D_1(\alpha) = \alpha^2 = \left(\frac{K}{2X}\right)t \quad \boxed{4}$$

2x is the thickness of the reactive layer. This equation can also put in the form:

$$D_1(\alpha) = 0.25\left(\frac{t}{t_{0.5}}\right) \quad \boxed{4}$$

the reactions controlled by a two-dimensional diffusion in a cylinder of radius r obey to the equation of J.B.Holt[18]

$$D_2(\alpha) = (1-\alpha)Ln(1-\alpha)+\alpha = \left(\frac{K}{r^2}\right)t = 0.1534\left(\frac{t}{t_{0.5}}\right) \quad \boxed{5}$$

Most analyzes data given by Valensi [17] reduce to the equation ⑤ when the volume of the obtained product is the same as the original matériau. The equation given by Jander [] on a diffusion controlled by symmetry shérique takes the following form:

$$D_3(\alpha) = \left[1-(1-\alpha)^{1/3}\right]^2 = \left(\frac{K}{r^2}\right)t = 0.0426\left(\frac{t}{t_{0.5}}\right) \quad \boxed{6}$$

3.2.3. Reactions controlled by diffusion in the gain boundaries

If the reaction is controlled by the movement of a constant velocity μ to interface. The equation that relates α to t may then be derived from a simple geometric form. Example for a circular disc or a cylinder we obtained

$$R_2(\alpha) = \left[1-(1-\alpha)^{1/2}\right] = \left[\frac{\mu}{r}\right]t = 0.2929\left(\frac{t}{t_{0.5}}\right) \quad \boxed{7}$$

for a sphere of radius reacting from the surface:

$$R_3(\alpha) = \left[1-(1-\alpha)^{1/3}\right] = \left[\frac{\mu}{r}\right]t = 0.2063\left(\frac{t}{t_{0.5}}\right) \quad \boxed{8}$$

3.2.4. kinetic equations based on the concept of reaction order

Analytically it is most convenient to use an equation:

$$\frac{d\alpha}{dt} = (1-\alpha)^n \quad \boxed{9}$$

which also applied in the case of reactions in the solid state for some values of n. The integration of the equation ⑨ led to some equations already explained. When n = 1/2 the integrated equation ⑨ gives equation ⑦ as well as n = 2/3 we obtain equation ⑧.

Sometimes some reactions in the solid state follow a first-order kinetic law n=1. The integrated form of the equation ⑨ is

$$F(\alpha) = \ln(1-\alpha) = -Kt + C = \frac{0.693}{t_{0.5}} \quad \boxed{10}$$

for other values of n other than 1; 2/3; 1/2 the obtained equations have no physical signification

3.2.5. Reactions controlled by nucleation in the gain boundaries

The mechanism controlling the reaction in the grain boundary assumed that the germination starts only when the surface of each particle is covered with a product layer. However the process of germination can occur at random and cannot be followed by an increase of the surface. When the germs grow they come up against with each other this phenomenon stops when some touch. This process has been studied by Avrani[19] and Erofe'ev [20] who proposes the following equations:

$$A_2(\alpha) = [-\ln(1-\alpha)]^{\frac{1}{2}} = Kt = 0.8326\frac{t}{t_{0.5}} \quad \boxed{11}$$

$$A_3(\alpha) = [-\ln(1-\alpha)]^{\frac{1}{3}} = Kt = 0.8850\frac{t}{t_{0.5}} \quad \boxed{12}$$

3.3 Experimental Measurements

3.3.1.First hydriding kinetic

The compound $TiFe_{0,5}Co_{0,5}$ absorbs hydrogen at 25°C under a pressure of 4MPa, 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)
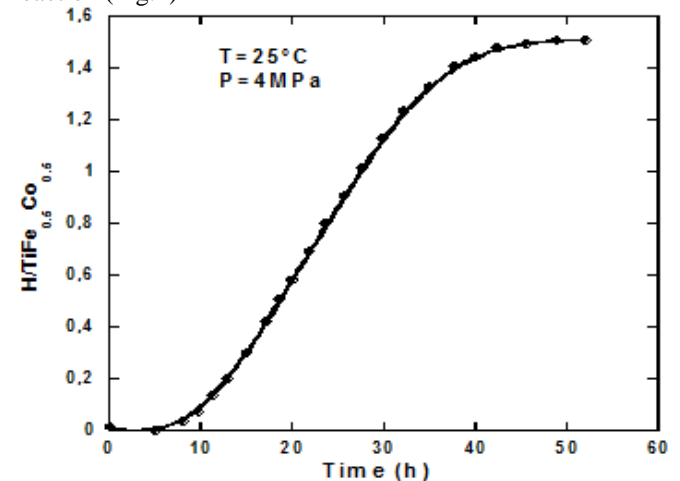

Figure 1: Kinetic of first hydrogen absorption by $TiFe_{0,5}Co_{0,5}$

In a previous study [3] we showed that a preliminary treatment of the sample (10^{-5}Pa vacuum at 200°C) leads to the disappearance of the latency period and an acceleration of the rate of sorption hydrogen. 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. These results are in good agreement with those found in the literature [16].

3.3.2. Isothermal and isobaric kinetic curves

After activation of the sample a series recorded curve translated in rate of progress (ξ = f (t)) were performed at temperatures ranging from 65 to 115°C and at pressures ranging from 0,7 to 3 MPa the rate of progress of the reaction is defined as follows: $\xi = n_H/n_\infty$ where n_H is the number of hydrogen atoms fixed by the alloy at time t and n_∞ the final number of atoms fixed after a very large time. Family of isothermal and isobaric curves corresponding to the hydrogenation of $TiFe_{0,5}Co_{0,5}$ are shown in Figures 2 and 3.
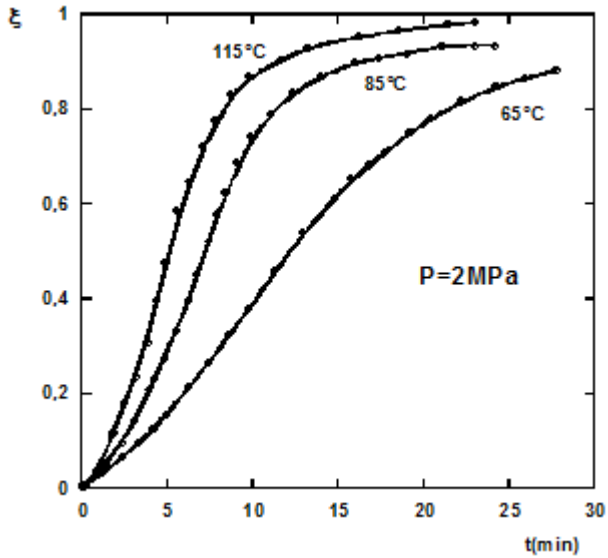
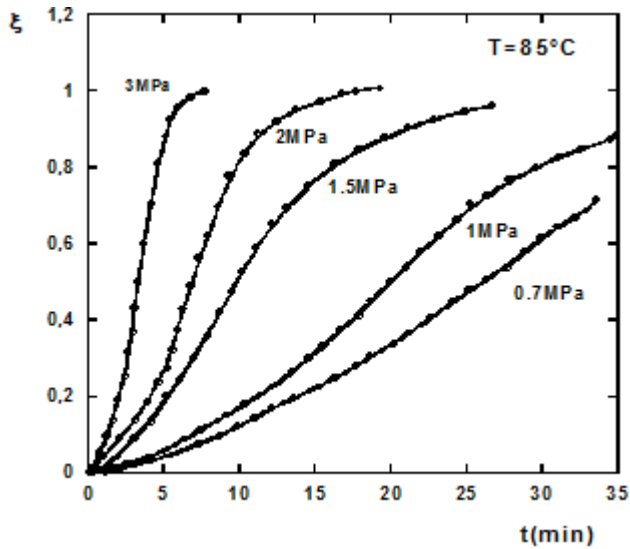**Figure 2:** Isobaric curves at different temperatures

Figure 3: Isothermal curves at different pressures

All these curves are sigmoidal with an inflection point at t=0.5 and will overlap in a same affinity relative to time reduced t /$t_{0.5}$(fig.4). This suggests that the processes controlling the kinetics of hydride formation reactions is the same. The affine sigmoid curve of Figure 4 can be divided into three domains each translate a mechanism. First domain very narrow whose concavity is oriented upward corresponding to the appearance of first germs on potential sites.
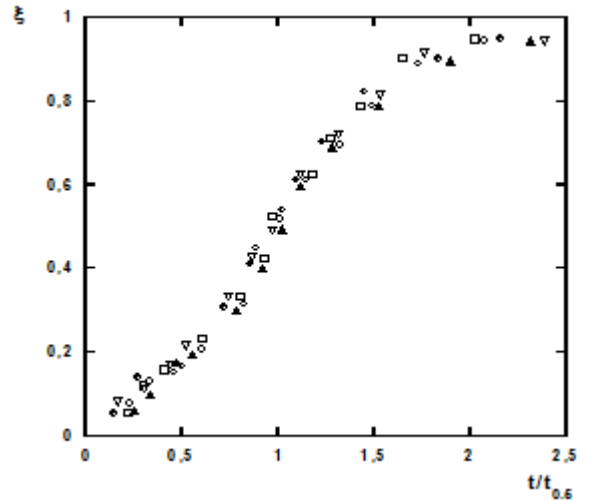

Figure 4: Affinity of the isothermal curves as a function of the reduced time

(●:0.7MPa), (▲: 1MPa), (○:1.5MPa), (□: 2MPa), (∆: 3MPa)

Second domain very large range of almost linear shape corresponding to both germination and growth. In the third domain germs become large enough and collide with each other, which leads to a slowing of the rate of reaction and limits the diffusion of hydrogen in the mass of the solid. On the other hand isotherms and isobaric experimental curves are suitably linearizing in the equation of Johnson and Mehl [21] for values of x ranging from 0.15 to 0.85 as shown in figure5. $[-\ln(1-\xi)]^{1/2} = \frac{K_i}{a_i}t$. Such an equation reflects a mechanism witch controlled by nucleation and growth (K_i is the interfacial velocity and a_i the average radius of the grains)
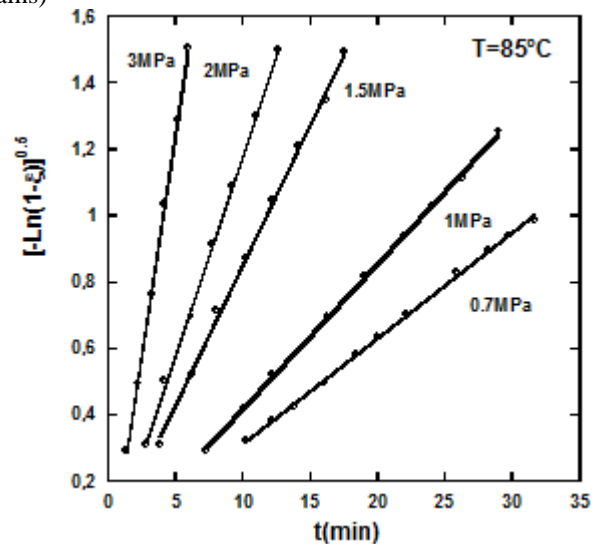

Figure 5: Linearization of sigmoidal curves into the equation of Johnson and Mehl [21]

3.2.3. Exploitation results of kinetic curves

the variations of the instantaneous speed $V_{0.5}$ depending on the deviation from the equilibrium pressure (fig.6) are linear and can be expressed in the following form:

$V_{0.5} = \frac{K_i}{a_i}(P_{H2} - P_e)$ the speed interfacial K_i is function of the parameters sample such as: the period, the frequency of cycles, the size ....etc.
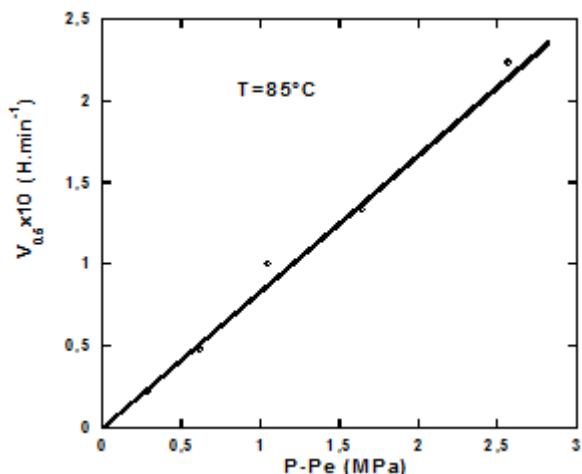
Paper ID: SUB1520

466

Figure 6: Variation of the instantaneous speed as a function of the deviation from the equilibrium pressure

P_e designates the equilibrium pressure for which the speed is zero, if the term K_i follows the law of the Arrhenius the rate equation $V_{0.5}$ becomes: $V_{0.5} = \frac{K_0}{a_i} e^{-\frac{Ea}{RT}}(P_{H2} - P_e)$, Ea is the apparent activation energy for the conversion of $TiFe_{0,5}Co_{0,5}$ into hydride, it can be deduced from the graph $ln\frac{K_i}{a_i} = f\left(\frac{1}{T}\right)$ represented in figure.7
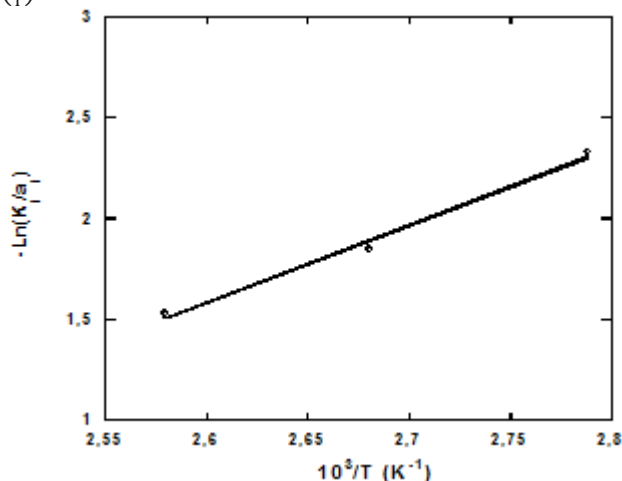

Figure 7: Determination of activation energy

Note that the values $\frac{K_i}{a_i}$ are the slopes of the straight lines of Johnson and Mehl [21] the activation energy obtained is Ea=30.2 KJ/mol.H_2

4. Conclusion

The kinetic study of hydrogen absorption by the TiFe compound has allowed us to draw some important results.
- Sample activation is easy, two cycles are sufficient to attain repeatability of experimental curves.
- The hydrogenation reactions are fast
- The curves of the hydride formation reactions are sigmoidal form and can be transformed into straight according to the johnson and mehl equation which reflects a mechanism controlled by the nucleation and growth.
- A logical continuation of this work is to study the evolution of the grain size with the number of cycles and also the mechanical stress caused by the loading of the alloy by hydrogen

References

[1] Thompson P, Reilly JJ, Hastings JM. The application of the Rietveld., J Appl Crystallogr 1989;22:256–60.
[2] Reilly JJ, Wiswall Jr RH., Inorg Chem 1974;13(1):218–22.
[3] M.Boulghallat, A.Jouaiti, A.Lâallam, International Journal of Sciences and Research, vol.3, issue 12, 2014 pages 904-908
[4] E.D.Koultoukis, S.S. Makridis, L.Röntzsch, E.Pavlidou, Journal of Nanoscience and Nanotechnology, Vol. 12, 4688–4696, 2012
[5] Asheesh Kumar, Seemita Banerjee*, C.G.S. Pillai, S.R. Bharadwaj, international journal of hydrogen energy 38(2013) 1335- 13342
[6] A.Kinaci, M.K.Aydinol*.,International Journal of Hydrogen Energy 32 (2007)2466– 2474
[7] Moegamat Wafeeq Davids a, Mykhaylo Lototskyy a,*, Alexander Nechaev b, Qiling Naidoo b, Mario Williams a, Yevgeniy Klochko International Journal of Hydrogen Energy 3 6(2011) 9743-9750
[8] Uchida H., International Journal of Hydrogen Energy, 24(1999)861-869.
[9] Feng F, Northwood DO., International Journal of Hydrogen Energy, 29(2004) 955-960.
[10] Wunder VK, Schmid S, Popovska N, Emig G. MOCVD., Surf Coatings Tech 151-152 (2002) 96-99.
[11] E.Bershadsky, Y.Josephy, M.Ron., Journal of the Less Common Metals, 172-174, part3,1991 pages 1036-1043
[12] Billur Sakintuna a, · , Farida Lamari-Darkrim b, Michael Hirscher c ., International Journal of Hydrogen Energy Volume 32, Issue 9, June 2007, Pages 1121–1140
[13] T.B.Flanagan, « Hydride for Energy Storage » Proceeding for an International Syposium, Geilo(Norway) , (1978) 135-150
[14] J.H.Charp, J.Y.Lee., Journal of the Less Common Metals, the role of diffusio in cataysis Addision-Wesley, Reading Massachussets (1975)
[15] G.Valensi, Journal de Chimie Physique 47(1950) 489
[16] J.Suzuki M.Abe, J. Less. Common. Met., 131(1987)301-309
[17] Gabrie Valensi, kinetics of oxidation of metallic spherules and powder , Compt. Rend., 202 (4) (1936) 309-12
[18] J.B.Holt, I.B.Culter and Wadswotth., rate of termal dehydratation ok kaolinite in vaccum J. Am.Ceram.Soc.45 (3) (1962) 133-36
[19] M.Avrami, kinetics of phase change., J.Chem.Phys., 7 (12) 1939) 1103-12
[20] B.V.Erofe'ev ., generalized equation of chemical kinetics and its application in reaction involving solids Compt.rend.Acad.Sci.URSS., 52(1946) 511-14
[21] W.A.Johnson, R.F.Mehl., Trans. Am.Inst.Min.Eng.135 (1939) 451

Author Profiles

Mustapha BOULGHALLAT, University of Sultan Moulay Slimane, Faculty of Sciences and Technoloqy, Department of Chemistry and Environment, Beni Mellal, Morocco. Master of

Paper ID: SUB1520

Chemistry (1987) at the University of MohammedV, Rabat (Morocco). Ph.D. Physical Chemistry (1992) at the University of Bourgogne, Dijon (France). Assistant teacher at the Lycée Saint Joseph, Dijon (France) 1989-1990.Visiting lecturer at the University of Bourgogne, Dijon(France) 1990-1992. Visiting lecturer at the Technological Institute University of Bourgogne, Dijon (France) 1992-1994. Professor Assistant at the Faculty of Sciences and Technoloqy of Beni Mellal (Morocco)1995-2003. Professor at the Faculty of Sciences and Technology of Beni Mellal (Morocco) since 2003. Member of laboratory Sustainable Development. Team responsible of Corrosion and treatment of materials. Research interests are Solid-gas reactions, Corrosion and protection of materials, Kinetic ,catalysis and thermodynamic Analytical control

Ahmed JOUAITI, University of Sultan Moulay Slimane, Faculty of Sciences and Technology, Department of Chemistry and Environment, Beni Mellal, Morocco. Master of physical (1987) at the University Cadi Ayyad, Marrakech (Morocco), Ph.D. Physical Chemistry (1994) at the University of Strasbourg, (France). Professor Assistant at the Faculty of Sciences and Technology of Beni Mellal (Morocco)1996-2003, Professor at the Faculty of Sciences and Technology of Beni Mellal (Morocco) since 2003, Member of laboratory Sustainable Development, Team member of Corrosion and treatment of materials. Research areas are Diffusion phenomena, Surface and interface, Modeling of physical and chemical systems.