

Mechanism and Kinetics of Hydrogen Diffusion in Some $Zr(Cr_{1-x}Fe_x)_2$ Laves phase

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Abstract: A series of $Zr(Cr_{1-x}Fe_x)_2$ alloys with $x=0.4, 0.6$ and 0.75 were prepared the major phase in these alloys had C14 Laves phase type structure. Experiments were carried out in a microbalance with a high sensibility (2.10^{-6} g) at different supply pressures (0.05 to 1MPa) and absorption temperatures (20 to 70°C) in a close system. The microthermogravimetry method was applied to interpret the experimental data and to compare with each other approach and its possibility were discussed. The maximum hydrogen storage capacity of these compounds varies between 2.5 to 2.85 (H/formula). Absorption-desorption kinetics of the hydrides was realized on a sample mass equal to 50mg in the aim to minimize the heat gradient. After activation period the kinetics were found to be fast and vary linearly with the pressure values. The reactions rate are controlled by nucleation and growth in the formation and by three-dimensional diffusion outside the grains in the decomposition. Activation energy values in the above-mentioned alloys were found respectively equal: E_a 44.3, 50.2 and 54.5KJ/mol.H₂

Keywords: Laves phases, hydriding, dehydriding, activation, kinetic, mechanism, nucleation

1. Introduction

The adsorption of hydrogen on the metallic surface appears to an important preliminary step in the kinetics of hydriding alloys. However, this surface presents an inhomogeneity which often is due to the formation of very thin oxide layers in the sample.

The hydrogen dissolves into the metal system in atomic form must first to dissociate on the surface of reaction $H_2 \rightleftharpoons 2H$ the dissociation energy is great enough (426KJ/mole) and represents an energy barrier that slows the reaction rate. The molecule that adheres to the surface must dissipate its energy in a vibrational and rotational and is chemisorbed.

After migration of the surface the atomic hydrogen penetrates in the first layer and diffuses into the metal lattice. We cannot say beforehand what the longest step is, or determine the reaction rate. For desorption of hydrogen atoms diffuse towards the surface, penetrate the first layer and reach the chemisorbed state. Before being able to leave the surface, these atoms must recombine on molecule and migrate to the surface (associative desorption)

The kinetics work on ZrB_2 Laves phase (with B= transition metal) have long been the subject of several research [1],[2],[3],[4] using various methods, the most obtained results show the importance of the surface state which determining the mechanism of hydrogen diffusion and the reaction rate. Other investigations [5],[6],[7],[8] on $Zr(Fe_xCr_{1-x})_2$ compounds suggest that the absorption rate of hydrogen begins slowly then speeds up when the reaction progresses and the germination is the limiting step.

It was found [9], [10] ,[11] that these kinetic and thermodynamic properties were highly dependent on the solid solution in atomic site of A or B. The hydrogenation properties are explained based on the composition, the alloying element, and the free cell volume of the hydrides.

The model proposed [12],[13],[14] assumes that the initiation of the growth process can take place only at certain sites, with, with a limited number of such sites avail on the surface. Also the probability for the start-up of the growth process increases with increasing super saturation of the hydrogen concentration at these sites. The interplay between these two factors (i.e., available) evolution of the relative amounts and the unit cell volumes of the α and β phases at transients, shows that for surface-treated and activated materials, the main rate limitation is the kinetics of the $\alpha \rightleftharpoons \beta$ phase transformation, i.e. the mobility of the phase interface and not the diffusion coefficient of the hydrogen in the phases (here deuterium, for neutron diffraction reasons). Dehydriding kinetics of nanoparticles [15] depend on the particle size and limited by associative desorption of hydrogen from the surface layer. The apparent kinetics is relatively slow in the later stage. The aim of the research [16] to understand decomposition of hydrides of metals and determine the most significant limiting reactions one function that describe real physical process was used. It was shown that nucleation and growth typical for non metallic, while for metallic ones the "shrinking core" morphology is more common.

2. Experimental Details

The compounds are prepared by direct arc melting under argon atmosphere of the pure components in stoichiometric proportions. The samples are made homogeneous by several remelting and are annealed. The compounds are checked by microprobe analysis. Micrographics show that they are single phased. The hydrogen used is the (U) quality of Air Liquide and is made free of residual water and oxygen traces by passing it through cartridge of molecular sievet .All the thermodynamic and kinetic experiments are carried out by microthermogravimetry 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

The kinetics of the metal hydrides has been investigated in order to map the reaction mechanisms of hydrogen absorption and desorption and to identify possible rate limiting steps to improve the kinetics. The reaction kinetics is greatly influenced by temperature and pressure but mostly, the hydriding-dehydriding kinetics are investigated with the influence of temperature in order to determine the reaction rate and mechanism [17], [18]

3.1 Samples Activation

The activation and surface state are generally two major factors that play a very important role in studies of the interaction gas-metal. The presence of oxide or hydroxide on the metal surface [19] inhibits or slow the reaction kinetics, reducing passivation of this surface by heat treatment of the sample is the first stage of activation. In the case of alloys studied in this work this step is easily achieved. The first hydridation of $Zr(Cr_{1-x}Fe_x)_2$ alloys is obtained at 25°C under an H_2 Pressure of 2.5MP. Figure.1 shows the curve's kinetic of the first hydrogen absorption by the $Zr(Cr_{0.4}Fe_{0.6})_2$ compound. The transformation begins after an induction period of approximately 15min and requires ten hours of reaction leading to the final composition 2.7H/mol. The other compounds $Zr(Cr_{0.6}Fe_{0.4})_2$ and $Zr(Cr_{0.25}Fe_{0.75})_2$ absorb respectively 2.85 and 2.5 H/mol. After a first cycle of hydriding-dehydriding grain size ranges 50 to 100 μ m, then changing over the following cycle until a limit value of 10 μ m.

The 2nd and 3th hydridation are achieved in time unless than one hour and without induction period. Figure.2 From the third absorption-desorption cycle the reaction rate is becomes constant. The alloys can be considered to be activated.

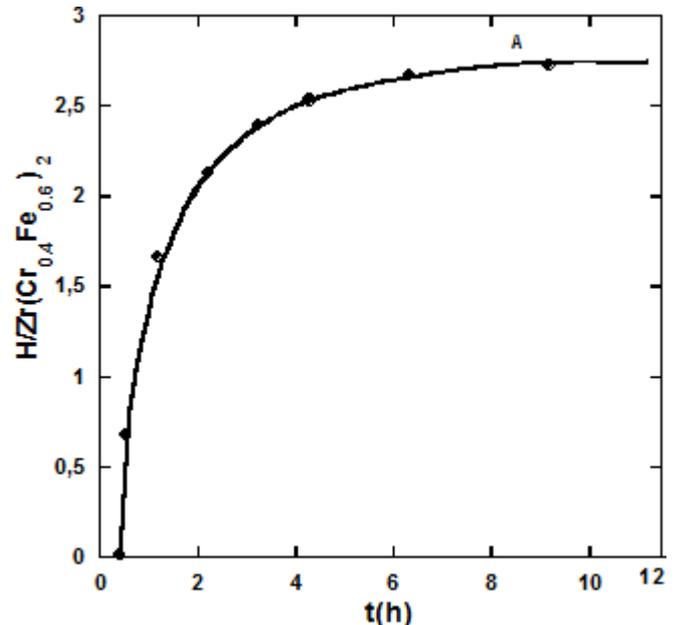


Figure 1: kinetic of the first hydridation of $Zr(Cr_{0.4}Fe_{0.6})_2$ compound.

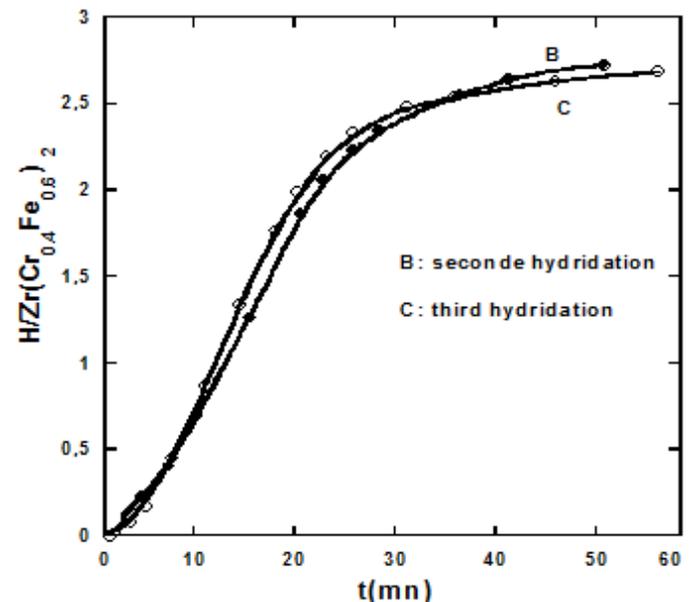


Figure 2: Kinetics activation of the $Zr(Cr_{0.4}Fe_{0.6})_2$ sample

3.2 Kinetic results

The kinetic curves of formation and decomposition performed at different pressures and different temperatures were carried out on samples already activated.

3.2.1 Formation kinetics

The hydriding curves ξ versus time (in which ξ is the transformed fraction n_H/n_{∞}) of the $Zr(Cr_{1-x}Fe_x)_2$ compounds performed at $T=70^\circ C$ under $P_{H_2}=1MPa$ are sigmoid with an inflexion point near 0.5. Such a family of curves is represented in Figure.3. These curves are correctly transformed into straight lines as shown in Figure.4 by the equation of Johnson and Mehl [20]: $-\ln(1-\xi) = K_f t^2$; (K_f : constant rate of formation; t : reaction time). This equation represents a mechanism controlled by nucleation and growth of new phase.

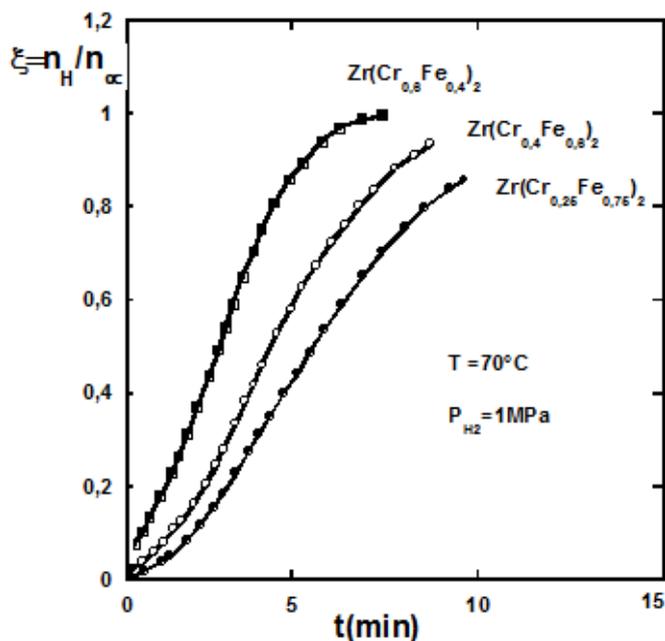


Figure 3: formation kinetic curves of $Zr(Cr_{1-x}Fe_x)_2$ compounds

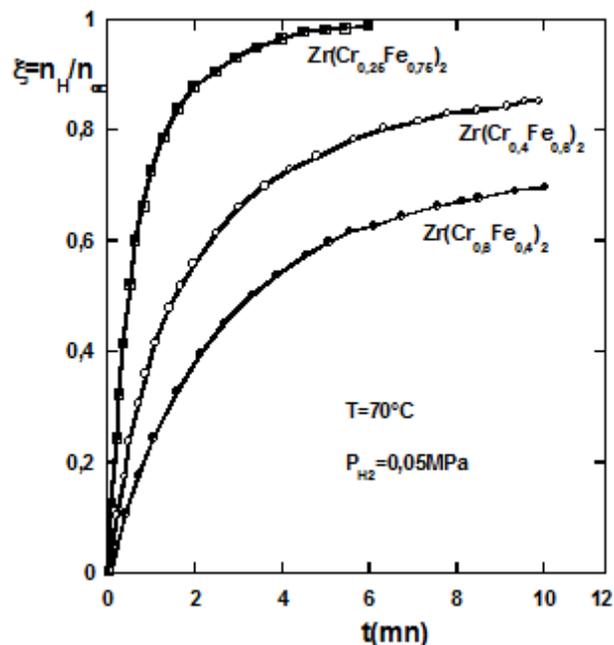


Figure 5: decomposition kinetic curves of $Zr(Cr_{1-x}Fe_x)_2$ compounds

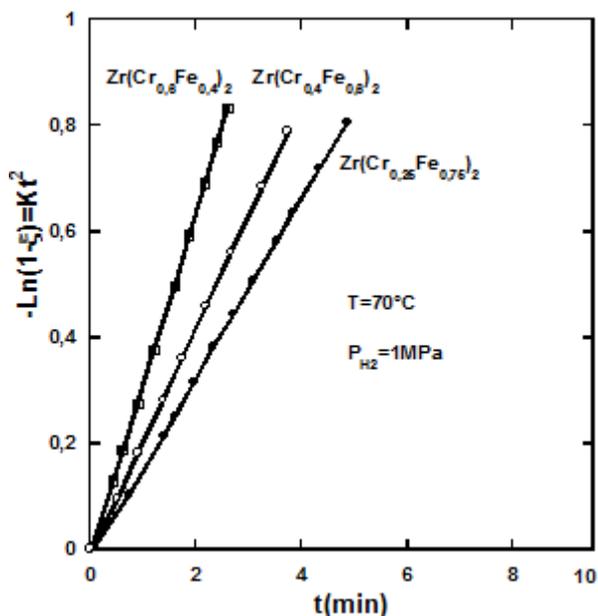


Figure 4: linearization of formation kinetic curves in Johnson and Mehl [20] equation

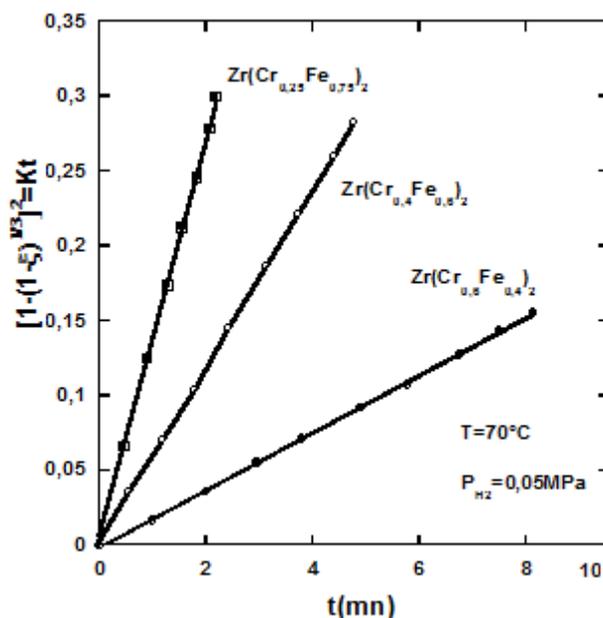


Figure 6 : Transformation of decomposition kinetic curves into straight lines in Jander's equation

3.2.2 Decomposition kinetics

The study of the decomposition kinetics of the hydrides formed were carried out at $T=70^{\circ}C$ under $P_{H_2} = 0.05MPa$ the obtained curves represented in Figure.5 are continuously decreasing rates versus time, these curves are well transformed into straight lines (Figure.6) when they are expressed in Jander's equation [21]: $[1-(1-\xi)^{1/3}]^2 = K_d t$; (K_d : constant rate of decomposition). Such an equation represents a system in which the regulating step is three-dimensional diffusion of hydrogen to outside of the grains.

3.2.3 Role of the temperature

A series of formation-decomposition curves under constant pressure ($P_{H_2} = 1 MPa$ in formation and $P_{H_2} = 0.05 MPa$ in decomposition) have been recorded at different temperatures (between 25 and $90^{\circ}C$), in order to determine the apparent activation energy E_a . Figure.7 gathers the curves $\ln K_f = f(1/T)$ of the three compounds studied. By analogy with the relationship $\ln P_e = f(\text{cell volume})$ that we have already established in a recent work [22] we also found that the activation energy E_a varies linearly with the unit cell volume in the opposite direction during formation and in the same direction during the decomposition. (Figure.8).In effect, the less voluminous compound shows a higher equilibrium pressure but its reaction rate is slow, therefore requires high activation energy.

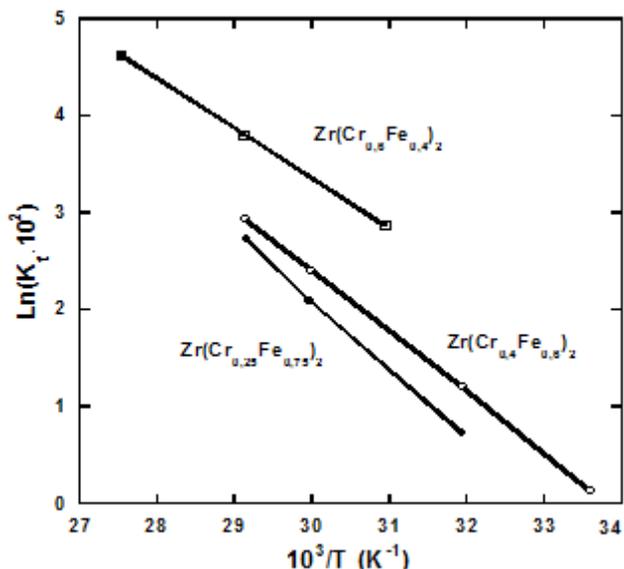


Figure 7 : Evolution of constant rate logarithm versus 1/T

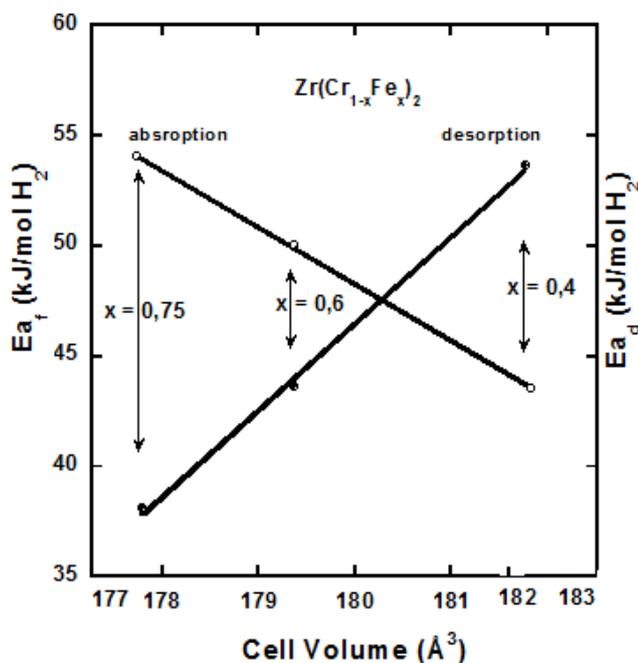


Figure 8: variation of activation energy in $Zr(Cr_{1-x}Fe_x)_2$ hydrides versus cell volume

All physicochemical parameters derived from this study are summarized in the table below.

$Zr(Cr_{1-x}Fe_x)_2$	$V(\text{\AA})^3$	H/metal	P_{ef} (MPa) at 70°C	P_{ed} (MPa) at 70°C	Ea_f (KJ/mol.H ₂)	Ea_d (KJ/mol.H ₂)
x=0.4	181.75	2.85	0.1	0.075	44.3	50.4
x=0.6	179.45	2.7	0.45	0.31	50.2	41.8
x=0.75	177.80	2.5	1	0.65	54.5	38.0

(P_{ef} : equilibrium pressure, Ea_f : activation energy) in formation

(P_{ed} : equilibrium pressure, Ea_d : activation energy) in decomposition

4. Conclusion

It appears from this study on the hydriding-dehydriding kinetics of $Zr(Cr_{1-x}Fe_x)_2$ alloys that the reactions of formation and decomposition are respectively controlled by the nucleation and growth and the three-dimensional diffusion outside the grains. By analogy with a recent study [22] that we have established a relationship between thermodynamic and structural parameters, this study also allowed us to reveal a correlation between kinetic parameters and structural of $Zr(Cr_{1-x}Fe_x)_2$ alloys. As a result increasing x causes a reduction of (cell volume, stability of hydride, storage capacity, formation rate) but against an increase in (hysteresis factor, decomposition rate). However, by varying x from 0.4 to 0.75 it has noticed any change on the structure of alloys or on their kinetic mechanism.

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