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HYSTERESIS AND SLOPING PLATEAU PRESSURES
IN Zr(Fe\textsubscript{x}Cr\textsubscript{1-x})\textsubscript{2} - H SYSTEMS

by

Shenghua Qian

A Dissertation
submitted to the Faculty
of Graduate Studies and Research
through the Department of Engineering Materials
in Partial Fulfillment of the requirements
for the Degree of Doctor of Philosophy
at the University of Windsor

Windsor, Ontario, Canada
1989
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ABSTRACT

Zr(Fe,Cr_{x1-x})_{2} (x = 0.5-0.8) alloys are promising hydride forming materials with various applications. Pressure-composition isotherms for Zr(Fe,Cr_{x1-x})_{2}-hydrogen systems are determined over temperature range 283.2 to 352.2 K in a accurate Sieverts'-type apparatus developed for this investigation. Pronounced hysteresis and sloping plateaus are observed. The degree of hysteresis decreases with increasing temperature, increases with Fe substitution for Cr and increases when determined with small aliquots. Hysteresis and sloping plateaus are reduced during the first few cycles of hydriding and dehydriding and they increase after the sample is exposed to air. The hysteresis factors, \( \frac{1}{2}RT\ln{P_{f}/P_{d}} \), range from 217 J/mol H for x = 0.5 at 343.2 K to 1169 J/mol H for x = 0.8 at 283.2 K. The plateau slopes, d(lnP)/(H/M), are about 0.9 for hydride formation and range from 0.5 to 1.1 for hydride decomposition.

Hysteresis and sloping plateaus have important effects on the application of hydride forming materials. A comprehensive and critical literature review reveals the complexity of hysteresis and sloping plateaus in metal-hydrogen systems and the existing theoretical models seem not to be adequate to explain the experimentally observed behavior. A model is proposed to identify the nature and origin(s) of hysteresis
and sloping plateaus in metal-hydrogen systems, and the effects of temperature, composition, aliquot size, cycling, annealing and particle size are explained. In general, both elastic and plastic accommodation energies in both hydride formation and decomposition contribute to hysteresis and affect plateau slopes. For soft materials with ideal plastic behavior the elastic energy after plastic relaxation is small and the plastic energy is the major cause of hysteresis. For highly strain-hardening materials and brittle materials [most intermetallic compounds including Zr(Fe, Cr_{1-x})_2], the elastic component dominates the total accommodation energy and hysteresis is primarily a consequence of the elastic strain energy.
To

My Grandmother
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NOMENCLATURE

\( a \)  spherical precipitate radius
\( d \)  Bragg plane spacing
\( d^* \)  equal to \( 2 \sin \theta/\lambda \)
\( D \)  crystallize size
\( E_C \)  activation energy for chemisorption
\( E_{C,A} \)  activation energy for activated chemisorption
\( E_{C,NA} \)  activation energy for non-activated chemisorption
\( E_{HC} \)  heat of chemisorption
\( E_D \)  heat of dissociation
\( E_P \)  heat of physisorption
\( E_S \)  heat of solution
\( E_{el} \)  total strain energy in a purely elastic state per unit volume of precipitate
\( \Delta G_{accom} \)  total accommodation energy per mole of precipitate
\( \Delta G_{inter} \)  molar interfacial energy
\( \Delta G_{def} \)  energy contribution of defects
\( \Delta G^N \)  nucleation energy
\( \Delta G^G \)  growth energy
\( \Delta G_f \)  molar free energy change for hydride formation
\( \Delta G_d \)  molar free energy change for hydride decomposition
\( \Delta G_{chem} \)  molar chemical free energy change
\( \Delta G_{non-chem} \)  molar non-chemical free energy change
\( \Delta G_{el} \)  equal to \( E_{el} V \)
\[ \Delta G_E \] equal to \( W_{V_m} \)
\[ \Delta G_P \] equal to \( W_{P_m} \)
\[ \Delta G_{\text{abs}} \] energy barrier for dissociative adsorption
\[ \Delta G_{\text{des}} \] energy barrier for associative desorption
\[ H/M \] hydrogen to metal ratio
\[ \Delta H \] enthalpy
\[ \Delta H_f \] enthalpy for hydride formation
\[ \Delta H_d \] enthalpy for hydride decomposition
\[ \Delta H_{\text{eq}} \] equilibrium enthalpy
\[ K \] bulk modulus of matrix
\[ K^* \] bulk modulus of precipitate
\[ P \] internal hydrostatic pressure in precipitate
\[ \bar{P} \] hydrostatic pressure due to effect of specimen size
\[ PC \] pressure-composition
\[ P_{H_2} \] hydrogen pressure
\[ P_{H_2}^0 \] initial hydrogen pressure
\[ P_f \] hydride formation pressure
\[ P_d \] hydride decomposition pressure
\[ P_{\text{eq}} \] equilibrium pressure
\[ P_{\text{Nf}} \] hydride formation pressure at nucleation stage
\[ P_{\text{Gf}} \] hydride formation pressure at growth stage
\[ P_{\text{Nd}} \] hydride decomposition pressure at nucleation stage
\[ P_{\text{Gd}} \] hydride decomposition pressure at growth stage
\[ P_{\text{sf}} \] hydride formation pressure measured by very small aliquot size
\( P_d^s \) hydride decomposition pressure measured by very small aliquot size
\( P_f^l \) hydride formation pressure measured by very large aliquot size
\( P_d^l \) hydride decomposition pressure measured by very large aliquot size
\( P_{f, min}^N \) minimum hydride formation pressure
\( P_{f, min}^C \) minimum hydride formation pressure at nucleation stage
\( P_{f, min}^G \) minimum hydride formation pressure at growth stage
\( P_{d, max} \) maximum hydride decomposition pressure
\( P_{d, max}^N \) maximum hydride decomposition pressure at nucleation stage
\( P_{d, max}^G \) maximum hydride decomposition pressure at growth stage
\( \Delta P \) equal to \( P_f - P_d \)
\( r_p \) plastic zone radius
\( \Delta S \) entropy
\( \Delta S_f \) entropy of hydride formation
\( \Delta S_d \) entropy of hydride decomposition
\( T_p \) hydride precipitate temperature
\( T_d \) hydride dissolution temperature
\( \Delta T \) equal to \( T_d - T_p \)
\( V_m \) molar volume
\( W \) total accommodation energy in elasto-plastic deformation per unit volume of precipitate
\( W_E \) total elastic energy in elasto-plastic deformation per unit volume of precipitate
$W_{E,\text{pp}}$ elastic energy in precipitate per unit volume of precipitate

$W_{E,\text{in}}$ elastic energy in plastic zone per unit volume of precipitate

$W_{E,\text{out}}$ elastic energy in elastic portion of matrix per unit volume of precipitate

$W_p$ plastic energy per unit volume of precipitate

$\alpha$ dilute solid solution

$\beta$ hydride phase

$\beta_T$ total integral breadth

$\beta_I$ instrument broadening

$\beta_S$ specimen broadening

$\beta_D$ crystallize size broadening

$\beta_C$ microstrain broadening

$\beta^*$ equal to $\beta \cos \theta_0 / \lambda$

$\theta_0$ Bragg angle

$\lambda$ wavelength

$\epsilon$ microstrain or misfit of precipitate

$\sigma$ specific interfacial energy

$\sigma_y$ yield stress in uniaxial tension

$\sigma_r$ radial stress component

$\sigma_B$ tangential stress component

$\sigma_e$ equivalent stress

$\nu$ Poisson's ratio of matrix

$\mu$ shear modulus of matrix

$\gamma$ equal to $K^*/K$
CHAPTER 1
INTRODUCTION

Many metals (alloys and intermetallic compounds) react reversibly with hydrogen to form metal hydrides. The reaction can be described in the simplified form as follows:

\[ M + \frac{1}{2} H_2 = \text{MH} + Q \]  \hspace{1cm} (1.1)

where \( Q \) is the heat of reaction and in most cases the hydrogen absorption process (hydride formation) is exothermic.

The thermodynamic aspects of the reaction 1.1 can be represented by pressure-composition (PC) isotherms. These curves are plots of hydrogen pressure \( P_{H_2} \) vs. composition (usually expressed by hydrogen to metal atom ratio: \( H/M \)) at various temperatures as shown in Fig. 1.1(a).

At low hydrogen concentrations there is a strong composition dependence of the hydrogen pressure. This region refers to the original metal phase which is able to dissolve generally a small fraction of hydrogen gas as a solid solution (\( \alpha \)-phase). As the hydrogen pressure, and thereby the concentration of dissolved hydrogen, is increased, nucleation and growth of the hydride phase (\( \beta \)-phase) start. Whilst the two phases \( \alpha \) and \( \beta \) coexist, the isotherms show a plateau,
i.e. hydrogen pressure remains constant as hydrogen composition is increased. This constant pressure is usually denoted as the plateau pressure and occurs in metal-hydrogen systems in the two types of phase diagrams (Fig. 1.2) [1]: a Miscibility Gap Type and a Structure Transformation Type. The coexistence of the two condensed phases may arise either from the presence of H-H attractions, which lead to a phase separation at low temperatures (Miscibility Gap Type) or from a structural difference between the metal and the metal hydride (Structure Transformation Type). Further increase of the hydrogen concentration, after the $\alpha$-phase has been completely converted into the $\beta$-phase, is again accompanied by a sharp increase in the hydrogen pressure. In most metal-hydrogen systems further pressure plateaus and hydride phases may be formed at higher hydrogen pressure.

The plateau pressure, which strongly depends on temperature, can be described approximately in a limited temperature range by

$$ \ln P_{H_2} = -2\Delta S/R + 2\Delta H/RT $$  \hspace{1cm} (1.2)

where $\Delta H$ and $\Delta S$ are the enthalpy and entropy per mole of atomic hydrogen of the phase transformation in the reaction (1.1). When $\Delta H$ and $\Delta S$ are taken to be temperature-independent in the limited temperature range considered, a so-called
van't Hoff plot of $\ln P_{H_2}^*$ versus $1/T$ yields the values for $\Delta H$ and $\Delta S$ (Fig 1.1(b)).

In practice, the PC isotherms show, to a greater or lesser degree, three non-ideal phenomena in the two phase region (Fig 1.3). These are: (1) Hysteresis: the time-independent "equilibrium" hydrogen pressure needed for hydride formation, $P_f$, is greater than that of hydride decomposition, $P_d$; (2) sloping plateau pressures: The hydride formation (decomposition) pressures are increasing (decreasing) during the phase conversion rather than being constant and (3) Gradual change of hydrogen pressure at the ends of plateau: Instead of being sharp cornered the PC isotherm flattens out and breaks away smoothly as the phase conversion begins and finishes.

The presence of these non-ideal phenomena indicates that the observed plateau pressures are not true equilibrium pressures and the reactions of hydride formation and decomposition are irreversible. In contrast to other irreversible processes, however, reversible behavior cannot be obtained even if the changes are carried out infinitesimally slowly. Nevertheless, the hydrogen pressure or free-energy change for each reaction is readily measurable and reproducible through many cycles of hydride formation/decomposition. PC isotherms in practice are the most useful way to represent the characteristics of metal-hydrogen systems and they have some thermodynamic
significance despite the irreversibility of the reaction. It is a challenge to find out the nature and the origin of, and to provide a thermodynamic description for, these non-ideal phenomena.

In recent years a large number of hydride forming materials (most are intermetallic compounds) have been developed with the following properties:

(1) Moderate pressure-temperature relations. Hydride formation/decomposition takes place at about room temperature and atmospheric pressure.

(2) High hydrogen content. The volumetric storage density exceeds that of liquid hydrogen (Table 1.1) [2].

(3) Large reaction heats.

(4) Rapid kinetics.

(5) Gas selectivity. The content of extraneous gas constituents in the desorbed gas is extremely low provided that the input gas is of a certain minimum quality.

(6) High sensitivity of hydrogen pressure against temperature.

These properties lead to various important applications, such as hydrogen-fuel storage for vehicles [2-4], isotope separation and removal of impurity gases [5-8], sensing and controlling devices [9], heat and fire detectors [10], hydride batteries [11], portable fuel cells and water pumps [12]. In particular, metal hydride technologies for the purification and compression of hydrogen [13-17] and for
energy conversion systems (thermal transformer, heat pumps and refrigerators) [16-24] have already been applied in industry and to commercial products.

Using hydride forming materials ultrahigh purity hydrogen can be obtained from industrial hydrogen. Ultrahigh purity hydrogen has found wide applications in the laboratory and in industry (Fig 1.4). Two kinds of metal hydride hydrogen purifiers have been developed. One can supply ultrahigh purity hydrogen at almost constant low pressures. It is also safer and has a smaller volume compared with a conventional high pressure hydrogen cylinder. The other combines the function of purification with compression to produce ultrahigh purity hydrogen at high pressures. The compression of hydrogen with metal hydrides involves only the heating of metal hydride, thus eliminating the source of contamination. A metal hydride hydrogen compressor has no moving parts and does not suffer from vibration. This also makes it attractive for use in a hydrogen refrigerator, especially when it is essential for measuring devices kept at about 20 K to have freedom from vibration [17]. Since thermal energy is used for the work of compression, the metal hydride hydrogen compressor may be driven by waste heat or solar energy.

A suitable pair of (or several pairs) of metal hydrides can be used for the construction of such energy conversion systems as thermal transformers, heat pumps and refrigerators. The advantages of metal hydride energy
conversion systems lie in the moderate hydrogen pressure-temperature relations of most metal hydrides where relatively low temperature heat (e.g. industrial waste heat) can be utilized for heating, steam generation and air-conditioning. A group of Japanese companies have developed a steam generation plant with metal hydride where steam at temperature level above 120°C is generated from industrial waste heat below 80°C [16]. High efficiency heating and air-conditioning units using metal hydride have also been developed in Japan and these units are intended for use in large commercial and industrial applications [16].

Another interesting example is the capture of liquid hydrogen boil-off with hydride forming materials [25]. A large amount of liquid hydrogen is vaporized during various operations at the Kennedy Space Center for the Space Shuttle Program. While the boil-off rates are too high for conventional recovery methods, hydride forming materials are fast enough to capture this low pressure boil-off hydrogen. The captured hydrogen can then be thermally compressed to higher pressures by hydride for reliquefaction. It is estimated that approximately 5.7 million liters of liquid hydrogen could be recovered which would result in annual savings exceeding $2 million.

In the applications of metal hydrides the non-ideal phenomena of hysteresis and sloping plateaus cause a loss of thermodynamic efficiency. Hysteresis and sloping plateaus are
particularly detrimental to the performance and efficiency of
metal hydride hydrogen compressor and metal hydride energy
conversion systems.

Fig 1.5 illustrates the working principle of a metal
hydride hydrogen compressor and how hysteresis and sloping
plateaus affect its operating efficiency. Hydrogen is
absorbed at low pressure $P_1$ and temperature $T_1$. Increasing
the temperature to $T_2$ hydrogen can then be released at higher
pressure $P_2$. When the hysteresis and sloping plateaus are
significant, however, the efficiency of compression is
reduced. At $T_1$ in order for hydride to be completely
saturated with hydrogen ($H/M$ reach $B$) hydrogen pressure must
be as high as $P_{r,b}(T_1)$ instead of $P_{eq}(T_1)$. When hydride is
heated to $T_2$, to release all the hydrogen stored in hydride
($H/M$ reduced to $A$) hydrogen pressure must be as low as
$P_{d,A}(T_2)$ instead of $P_{eq}(T_2)$. Obviously, the compression ratio
$P_{d,A}(T_2)/P_{r,b}(T_1)$ is much smaller than $P_{eq}(T_2)/P_{eq}(T_1)$.

To sum up, with the presence of hysteresis and sloping
plateaus and for a given reversible hydrogen content
$(\Delta(H/M)=(H/M)_B-(H/M)_A)$ hydrogen pressure for hydride
formation is raised from $P_{eq}(T)$ to $P_{r,b}(T)$ and hydrogen
pressure for hydride decomposition is reduced to $P_{d,A}(T)$. For
a metal hydride hydrogen compressor operating at $T_1$ and $T_2$
the compression ratio is lowered from $P_{eq}(T_2)/P_{eq}(T_1)$ to
$P_{d,A}(T_2)/P_{r,b}(T_1)$. And for metal hydride energy conversion
systems hysteresis and sloping plateaus will reduce the
pressure difference which is the driving force for hydrogen transfer between a pair (or several pairs) of metal hydrides at given operating temperatures or an achievable temperature level for a given pressure difference needed for efficient operation, thus severely affecting the performance and efficiency of the systems.

In this study, hysteresis and sloping plateaus in Zr(Fe, Cr, x-1)2-H systems are investigated. The hydriding properties of the Zr(Fe, Cr, x-1)2 intermetallic compounds have previously been explored in our laboratory [26]. These intermetallics are predominantly single-phase, having the C14 hexagonal MgZn2-type Laves phase structure, and are very brittle. Hydrogen is absorbed quite readily, with no special activation treatment. X-ray diffraction analysis revealed the formation of a distinctive hydride phase accompanying hydrogen absorption. Diffraction patterns of partial hydrided samples showed the co-existence of two condensed phases, indexed as the solid solution of hydrogen in the host metal and the metal hydride phase. During hydriding, the relative amount of the solid solution phase decreases and that of the hydride phase increases. The crystal structure of the host metal does not change when hydrogen dissolves, but the molar volume has about a 20% expansion when the hydride phase is formed. The host metal disintegrates into a fine powder with a mean particle size being about 10 μm during the first few hydride formation and decomposition cycles. Of these
intermetallics, Zr(Fe\textsubscript{x}Cr\textsubscript{1-x})\textsubscript{2} compares quite favorably to LaNi\textsubscript{5} in terms of hydrogen capacity, hydride stability and, most importantly, reaction kinetics.

The complete PC isotherms of hydrogen absorption and desorption and thermodynamic parameters for the two-phase region are determined for Zr(Fe\textsubscript{x}Cr\textsubscript{1-x})\textsubscript{2}-H systems (x=0.5, 0.6, 0.7 and 0.8). The effect of temperature, alloy composition, hydrogen aliquot size, hydrogen absorption and desorption cycling and surface contamination on hysteresis and sloping plateaus in these systems, and the lattice strain induced by hydride forming materials are examined. While the experimental work is performed mainly in Zr(Fe\textsubscript{x}Cr\textsubscript{1-x})\textsubscript{2}-H and LaNi\textsubscript{5}-H systems, the theoretical discussion covers all metal-hydrogen systems. Experimental observations of, and theoretical models for, hysteresis and sloping plateaus in metal-hydrogen systems are critically reviewed. A model is proposed to identify the origin of hysteresis and sloping plateaus in metal-hydrogen systems and to explain the experimental observations.
TABLE 1.1 Volumetric Density

of Hydrogen Storage by Various Media [2]

<table>
<thead>
<tr>
<th>Medium</th>
<th>Volumetric Density $N_H$ (atoms H/ml, $\times 10^{-22}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$ (liquid)</td>
<td>4.2</td>
</tr>
<tr>
<td>$H_2$ (gas at 100 atm)</td>
<td>0.49</td>
</tr>
<tr>
<td>MgH$_2$</td>
<td>6.7</td>
</tr>
<tr>
<td>FeTiH$_{1.74}$</td>
<td>5.5</td>
</tr>
<tr>
<td>LaNi$<em>5$H$</em>{6.7}$</td>
<td>7.6</td>
</tr>
</tbody>
</table>
Fig. 1.1 (a) Pressure-composition isotherms for idealized metal-hydrogen systems. (b) van't Hoff plot.
Fig. 1.2 Phase diagram types with hydrogen pressure plateaus [1].
Fig. 1.3 Illustration of PC isotherm of real metal-hydrogen systems.
Fig. 1.4 Hydrogen purification by metal hydride and its application [15].
Fig. 1.5 Working principle of a metal hydride hydrogen compressor and the effect of hysteresis and sloping plateaus on its operation efficiency. (a) PC isotherms; (b) van't Hoff plots.
CHAPTER 2
LITERATURE REVIEW

2.1 Hysteresis

2.1.1 Experimental Observations

Hysteresis seems to be an inherent feature of nearly all metal-hydrogen systems. There are three common manifestations of the hysteresis in a metal-hydrogen system (Fig.2.1):

i) Pressure hysteresis: Under an isothermal condition the pressure needed for hydride formation, $P_f$, is greater than that of hydride decomposition, $P_d$.

ii) Solvus hysteresis: The terminal solid solubility of hydrogen in the host alloy is greater for hydride formation than for hydride decomposition.

iii) Thermal hysteresis: At a given solvus composition the hydride formation temperature is lower than the hydride decomposition temperature.

Hysteresis is affected by different factors including temperature, alloy composition, hydrogen aliquot size, annealing of the metal sample, absorption/desorption cycling and particle size. The degree of hysteresis is usually described by one of the following four terms:

1) $P_f - P_d$;

2) $(P_f - P_d)/P_d$;

3) $P_f/P_d$ and ,
iv) $1/2RT \ln \left( \frac{P_f}{P_d} \right)$.

It has been argued that the last term, i.e. $1/2RT \ln \left( \frac{P_f}{P_d} \right)$, represents the Gibbs free energy loss per mole of atomic hydrogen in completing a hysteresis loop [27-29].

**The Effect of Temperature**

In most metal-hydrogen systems, the hysteresis effect, given as the ratio $\frac{P_f}{P_d}$, decreases with increasing temperature. The logarithmic function $1/2RT \ln \left( \frac{P_f}{P_d} \right)$, in general, also decreases with increasing temperature, especially at higher temperatures (see Table 2.1) [30-40]. At even higher temperature, hysteresis disappears [41, 42]. In uranium-hydrogen system the extent of hysteresis is very large at relatively low temperature, i.e. $1/2RT \ln \left( \frac{P_f}{P_d} \right) = 2.6 \text{KJ/mol H at 642K}$ [43] whereas at 723K this hysteresis in uranium hydride completely disappear [44].

The only exception in the published literature seems to be the experimental results on MmNi$_{5-x}$Al$_x$-hydrogen systems (Mm: Misch metal) [45]. Fig.2.2 shows the temperature dependence of hysteresis factor of MmNi$_{5-x}$Al$_x$-H systems at various Al-contents, where the magnitude of hysteresis is expressed by the factor $J$ which is the ratio of $P_d/P_f$. As temperature increases, $J$ deceases and hence the ratio of $P_f/P_d$ increases.
The Effect of Alloy Composition

Hysteresis effects differ in nature and magnitude from alloy system to alloy system. In some systems, the extent of hysteresis depends dramatically on the alloy composition whereas in other systems the hysteresis effect is relatively constant over a range of alloy composition. Table 2.2 summarizes the experimental measurements of the effect of alloy composition on hysteresis [26, 45-51].

For $V_xNb_{1-x}$-H systems [46] the hysteresis effect, as shown by the ratio of $(P_f/P_d)$, is about 2 for pure vanadium. As niobium is added, the hysteresis effect slowly increases until the composition approaches 50% Nb when there is an abrupt increase in $P_f/P_d$. At a concentration of about 80% Nb the values of $(P_f/P_d)$ rises to a maximum of 20. The hysteresis effect then decreases with increasing amount of Nb, reaching a value of 8 for pure Nb. Thermal hysteresis has also been observed in Nb-H system [52].

In $(La, Ce)Ni_5$-H systems, very large hysteresis effects have been observed [47]. The pressure difference $\Delta P$ between the hydride formation and decomposition pressures at 298K increases from approximately 1 atm for $LaNi_5$ to about 200 atm for $CeNi_5$. The addition of cobalt to $(La, Ce)Ni_5$ system markedly affects the PC isotherms and hysteresis. For example, in $(La_{0.5}Ce_{0.5})Co_xNi_{1-x}$-H system the substitution of nickel by cobalt reduces the hysteresis so that for x=1 (i.e. $La_{0.5}Ce_{0.5}Co_5$) the hysteresis has been reduced to
values typical of cerium-free LaNi$_5$-type compounds. The marked reduction in hysteresis effect is due mainly to the decreasing hydride formation pressure in the cobalt concentration range 0<X<1 since within this range of cobalt concentrations the hydride decomposition pressure remains almost constant.

The TiCrMn-H system displays a very large hysteresis effect [50]. The value of the hysteresis factor given by \( P_f/P_d \) is 3 at 263K. Increasing the titanium content or varying the Cr/Mn ratio in this alloy eliminates the large hysteresis effect, e.g. the \( P_f/P_d \) ratios for Ti$_{1.2}$CrMn, Ti$_{1.2}$Cr$_{0.8}$Mn$_{0.1}$ and Ti$_{1.2}$Cr$_{1.9}$Mn$_{0.1}$ are 1.15, 1.02 and 1.01 respectively (Table 2.2). The hysteresis in the PC isotherms for the Ti$_{1-x}$Cr$_x$Mn$_{1-2y}$ system \( 0.2 \leq x \leq 0.3, \ 0.5 \leq y \leq 0.8 \) [50] decreases markedly with decreasing manganese concentration. The marked reduction of the hysteresis effect is, unlike the \( \text{(La}_{0.5}\text{Co}_{0.5})\text{Co}_{x}\text{Ni}_{1-x} \) -H system, due primarily to an increase in the hydride decomposition pressure, with the hydride formation pressure staying virtually constant.

In the PdNi/H system [53], hysteresis seems to exist over the whole range of alloy composition. In the Pd/Pt/H system [53], however, the hysteresis effect at 298K tends to disappear for alloys containing >20% Pt.

The Effect of the Hydrogen Aliquot Size

It has been observed first in LaNi$_5$-H systems that the
plateau pressure for hydride formation or decomposition, and hence the hysteresis, depends on the size of the aliquot of hydrogen added or removed during PC isotherm measurements [54, 55]. When small aliquots of hydrogen are added or removed in the two-phase coexistence region, the plateau pressures for hydride formation and decomposition are higher and lower, respectively, than when large aliquots are employed (Fig. 2.3). Hysteresis is reduced when large aliquots of hydrogen are employed. It should be stressed that both plateau pressures determined by small and large aliquot size are time-invariant ones and in both cases equilibrium is apparently attained.

The effect on the plateau pressures and hysteresis due to aliquot size has also been found in two other intermetallic-H systems [56]: one is a miscibility gap system, ZrMn$_2$-H and one a structure transformation system, LaCo$_5$-H. It has been observed: 1) The hydrogen pressures for hydride formation decrease and those for hydride decomposition increase with increasing aliquot size. It seems that, however, there are limiting values for the effect of large aliquot size and the reduction of hysteresis trends to saturate. The employment of large aliquot size can not eliminate hysteresis. 2) The system can be moved from one type of plateau to the other. For example, when the system is on the large aliquot plateau $P_d$-branch, it can be moved to the small aliquot $P_d$-branch by removing small aliquots of hydrogen from the system.
Similarity the system can move from a small aliquot $P_f$-branch to the large aliquot $P_f$-branch by adding of a large aliquot of hydrogen. Table 2.3 shows the hysteresis for small and large aliquot plateaus, and the change observed in the free energy change of hydride formation using small and large aliquots for systems of $\text{LaNi}_5$-$\text{H}$, $\text{LaCo}_5$-$\text{H}$ and $\text{ZrMn}_2$-$\text{H}$, where the superscripts $s$ and $l$ for plateau pressure $P$ represents small and large aliquot size, respectively.

The Effect of Annealing

The effect of annealing of the activated hydrogen-free sample on the subsequent absorption and desorption pressures and hysteresis has been examined by both Flanagan et al [57] and Nomura et al [58] for the $\text{LaNi}_5$-$\text{H}$ system. Annealing effects start at rather low temperatures (Fig. 2.4); and the absorption pressure is found to increase dramatically following annealing (Fig. 2.5). The higher the annealing temperature before absorption, the higher the pressure of the subsequent absorption isotherm and hence the larger the hysteresis. The desorption plateau pressures are only slightly affected by the annealing treatment.

Using X-ray powder diffraction line profile analysis, Nomura et al [58] calculated the values of lattice strain after annealing of the dehydrided $\text{LaNi}_5$ sample at various temperatures. The lattice strain, as expected, was found to decrease with increasing annealing temperature. The lattice
strain was actually eliminated after annealing at a sufficiently high temperature. From these results they concluded that the lattice strain which exists in the activated powder reduces the absorption pressure and that the annealing treatment at high temperatures releases the lattice strain resulting in an increase in the absorption pressure.

In contrast to the behavior of LaNi₅, annealing of activated LaCo₅ does not significantly affect its behavior towards hydrogen [59]. It is probably worth noting that for LaCo₅ the plateau pressures can be readily measured without prior activation whereas for LaNi₅ the hydride phase will not readily form without an activation treatment. Although there are only a limited number of results upon which to base any conclusion, it appears that systems which require activation are affected by annealing of the activated sample whereas those which do not require activation are not significantly affected by annealing of the activated material.

The Effect of Absorption/Desorption Cycling

Fig. 2.6 shows PC isotherms for LaNi₅ at 353K on the first, second and third absorption/desorption cycle [58]. It can be seen that the absorption pressure decreases with increasing number of cycles whereas the desorption pressure remains almost constant. The hysteresis effect, therefore, decreases with increasing cycling. The similar effect of cycling on absorption and desorption pressures has been found
in Pd-H system [60, 61], U-H system [43], and SmCo₅-H systems [34].

In general it has been found that after about 5-10 absorption and desorption cycles, the exact number depending on the specific metal-hydrogen system, the absorption and desorption pressures, and hence the hysteresis effect, do not change anymore on further absorption and desorption cycles.

The effect of extended cycling (more than 1000 cycles involved) on hydriding characteristics of hydride forming materials has been investigated [62-72]. Two types of cycling were carried out: thermal cycling where the hydrogen absorption and desorption are induced by the change of sample temperature in a closed reactor; and pressure cycling where fresh hydrogen is introduced and removed for each cycle. While the cycling experiments are mainly focused on the kinetics and hydrogen absorption capacity some experimental results are available on the effect of cycling on the PC isotherms. Goodell [63] observed a significant change of PC isotherms for LaNi₅ which had undergone 1500 pressure cycles. The reaction plateaus increase in slope, decrease in pressure and split into two segments. Han and Lee [68] found similar, but less pronounced, results in their pressure cycling experiments on LaNi₅-H system. Kim and Lee [69] investigated the changes in hydrogenation properties of MnNi₄.₅Alₐ.₅ and MnNi₄.₁₅Feₐ.₈₅ induced by thermal cycling through PC isotherm measurement. They observed that the plateau slope and
hysteresis are slightly increased, whilst the plateau region is still retained after 3000 cycles. Reilly et al [70] reported an increased desorption pressure of FeTi-H system with increasing number of thermal cycles. The change in desorption pressures could be recovered by annealing.

The Effect of Particle Size

Wicke and Otto [43] have reported a decrease in the value of $\Delta P/P_f$ ($\Delta P=P_d-P_r$) at 642K for U-UH$_3$ system when the transformation from bulk uranium ($\Delta P/P_f=3.0$) to more finely divided uranium ($\Delta P/P_f=0.3$) occurs after a number of phase change cycles.

Everett and Sermon [73] found that absorption pressure for palladium black was smaller than that for bulk palladium, and the desorption pressure was raised for palladium black compared with bulk palladium. The hysteresis, therefore, is smaller for palladium black. It was also observed [74] that 50 nm Pd films exhibit smaller hysteresis than those of 300 nm.

For most intermetallic compound - hydrogen systems the host metal is disintegrated into a fine powder upon hydride formation and decomposition. The particle size decreases with increasing cycling. The decrease in particle size could be partially responsible for the effect of the first few cycles on hysteresis.

Kuijpers and van Mal [34] investigated a relationship
between particle size and the magnitude of hysteresis. They had an activated powder of LaNi$_5$ half saturated with hydrogen (corresponding with the mid-point on an absorption isotherm at room temperature). Vibrationary ball milling of the powder for 20 min in a hydrogen atmosphere, which reduced the particle size, did not result in a pressure decrease. It seems that the particle size in a well-activated powder (after 5-10 cycles) does not affect the magnitude of hysteresis.

The effects of different variables on the experimental observations of hysteresis are summarized in Table 2.4.

In addition to these major effects on hysteresis, the following experimental observations are worth mentioning.

(i) The hydrogen composition of the specimen must be changed above a certain minimum amount to demonstrate full hysteresis in the plateau region [17, 42].

(ii) The hysteresis effect varies widely (20% or more) from sample to sample [42], largely because of variations in hydride formation pressures. The hydride decomposition pressures obtained by various workers are generally in good agreement [75]. Furthermore, hydride decomposition pressure is usually well defined whereas formation pressure is not. Data obtained in hydrogen desorption are generally regarded as the best approximation to equilibrium between stable phases [34, 42, 76]. For the Pa-H system [77] difficulties in
the hydriding direction greatly exceed those for the reverse process and therefore effects in opposing directions cannot be assumed to have equal magnitudes. It is suggested that the equilibrium state for Pa-H system lies close to the dehydriding results.

(iii) Application of a suitable external stress would cause hydride precipitation [78-82]. External tensile stresses on the α phase increases the solvus temperature in Nb-H system [83, 84]. Applying an external stress to Mg₃NiH₄ induces its decomposition [85].

(iv) Many investigations into the kinetics of metal hydride formation and decomposition have shown that nucleation is the rate controlling step [86-90]. The nucleation and growth of hydrides in the Ti-10%Al alloy takes place only with difficulty [80]. The mechanical constraint on the hydride in the strong Al-Ti matrix may play an important role in the hydride nucleation and growth.

2.1.2 Theoretical Models

It was as early as in 1925 that Lanbert and Gates [91] described the a marked hysteresis effect in the Pd-H system. This was followed in 1933 by Bruning and Sieverts [31] who studied the phenomenon in greater detail. Since that time many explanations have been offered for hysteresis, see Table 2.5, but there still seems no general agreement as to its detailed origin.
Ubbelohde [92] proposed that the addition of hydrogen to the metal introduced strains and disorder in the metal which should be accounted for in the phase rule in the following manner:

$$F = C - P + 2 + \sum \Pi_i$$  \hspace{1cm} (2.1)

where \(\Pi_1, \Pi_2, \ldots\), represent additional degrees of freedom due to mechanical strains, state of disorder, surface energy, etc. The hydride phase (\(\beta\) phase) is strained and disordered due to the lattice expansion during the formation of this phase, which increases the absorption pressure. In desorption, the strain and disorder are relieved as hydrogen is removed, causing a lower desorption pressure. The theory, therefore, assumes that the desorption isotherm is associated with the ordered and strain-free form of the \(\beta\) phase, i.e. with the true equilibrium. This theory can explain hysteresis in a single phase region as has been observed in some metal-hydrogen systems [93].

Using a statistical mechanical approach in which the interaction energy between hydrogen atoms in a lattice is taken into account, Lacher [94] derived a theory which assigned metastable states to the \(\alpha\) and \(\beta\) phase. This resulted in oversaturation of the \(\alpha\) phase on absorption and undersaturation of the \(\beta\) phase on desorption. The true equilibrium, therefore, is situated in the mean region.
between the absorption and desorption branches of the hysteresis loop. Ubbelohde's modification of the phase rule was rejected by Lacher.

Wagner [95] proposed that the diffusion of metal atoms between the $\alpha$ and $\beta$ phase at lower temperatures is difficult in the two phase region compared to diffusion of the hydrogen atoms. This causes a non-equilibrium condition to exist during both absorption and desorption processes. The two conditions for equilibrium in a two-phase system are:

(i) the chemical potential of hydrogen in each phase must be equal;

(ii) the chemical potential of the metal must be equal in each phase.

The second condition cannot be satisfied because the metal atoms are not mobile at the temperature at which experiments are generally carried out. With this restraint removed, the phase rule should be written as $F=C-P+1$, thereby giving two degrees of freedom rather than one.

Libowitz et al. [96] proposed a defect theory to explain hysteresis. This theory assumes that there are non-stoichiometric vacancies in the lattice. As hydrogen is withdrawn from the stoichiometric hydride, hydrogen vacancies are formed, and the hydride becomes non-stoichiometric. At the composition where the lattice becomes saturated with vacancies further removal of hydrogen causes the lattice to break down, thus forming a two-phase system. Therefore, the
plateau pressure is actually the equilibrium pressure of non-stoichiometric hydride. On hydriding, it is possible, because of the longer time to reach equilibrium, that a rather stable metastable hydride is formed having fewer vacancies (higher hydrogen composition) than the stable hydride. The metastable hydride, because of its lower stability, has a higher plateau pressure. Since the hydriding phase has fewer vacancies, the hydriding curve on the P-T isotherm extends further to the right than the dehydriding curve. This would thus explain the solvus hysteresis.

Flotow et al. [97, 98] proposed a theory of hysteresis based on the size of the crystallites of α or β phase precipitating out of a matrix of the other during desorption or absorption, respectively. They argued that metal first formed on desorption of hydrogen from a hydride would be microcrystalline, while the metal absorbing hydrogen would be in a macrocrystalline form due to sintering. The difference between the size of the crystallites would give different enthalpies of reaction, thus causing differing hydrogen pressures on absorption and desorption. This theory seems limited to very special cases.

Everett and Nordon [99] analyzed their experimental results for hysteresis in Pd-H system in terms of Lacher's statistical mechanical theory, but they failed to obtain a fit of Lacher's equation to their data with a unique set of parameters. Different absorption and desorption isotherms
were derived which were dependent on different parameters. They assumed that the energies of absorption of hydrogen were different in the α and β phases, and that the interaction energy between hydrogen in the lattice of α and β phases is different. They proposed that the co-existence of both α and β phases over a range of pressures is probably associated with the large volume change accompanying the transition and concluded that no one reversible path between the two phases was possible, thus imposing an intrinsic pressure hysteresis on the system.

Scholtus and Hall [100] studied hysteresis in the Pd-H system and describe hysteresis in terms of internal stresses. Because of the large volume change which accompanies the α to β transition, plastic deformation of the α phase occurs as it is stretched beyond its elastic limit. Hence, absorption is accompanied by growth of the β phase under compressive stress of the α phase, but desorption takes place from the β phase of the plastically deformed solid. Since this is not a thermodynamically reversible process, hysteresis results. The desorption of only a small amount of hydrogen is all that is required to relax the residual elastic forces so that the phase is no longer under stress, then desorption occurs at lower transition pressure which corresponds to the true equilibrium. They called attention to the frequent experience that the plateau of absorption pressure is not well defined and that in particular the pressure increases with increasing
hydrogen content owing to the increase in mechanical strain. From the ratio of the absorption pressure to the desorption pressure they estimated the constraining pressure on the $\beta$ phase to amount to several kilobars. They argued that although Ubbelohde was correct in pointing out that the free energy of the $\beta$ phase is a function of the mechanical strain of the crystallites, this strain is related to hydrogen content and, therefore, cannot be incorporated into the phase rule as an independent variable.

Kuijpers and van Mal [34] proposed an explanation of hysteresis pertinent to LaNi$_5$-H and SmCo$_5$-H systems. They argued that the magnitude of the hysteresis is related to the rather larger volume expansion which accompanies the formation of the hydride. From their experimental results a correlation between the volume expansion on hydride formation and the magnitude of hysteresis expressed by $1/2RT\ln P_f/P_d$ can be established. Their analysis was generally derived from the theories of Everett and Nordon [99] and Scholtus and Hall [100] for the Pd-H system.

In studying hydride precipitation in Nb-H system, Birnbaum et al. [84, 101, 102] have attributed the thermal hysteresis to plastic deformation during both hydride formation and hydride decomposition. They have assumed that the molar free energy change on forming the $\beta$ phase from the $\alpha$ phase may be written as:
\[ \Delta G_{\alpha-\beta} = \Delta G^\text{chem}_{\alpha-\beta} + \Delta G^\text{elastic}_{\alpha-\beta} + \Delta G^\text{plastic}_{\alpha-\beta} + \Delta G^\text{surface}_{\alpha-\beta} \]  

(2.2)

where the first term corresponds to the free energy change on forming unconstrained \( \beta \) phase from the \( \alpha \) phase; \( \Delta G^\text{elastic}_{\alpha-\beta} \) and \( \Delta G^\text{plastic}_{\alpha-\beta} \) are the free energies associated with the elastic and plastic deformation due to the about 12% volume increase on forming the \( \beta \) phase; and \( \Delta G^\text{surface}_{\alpha-\beta} \) is a surface free energy term. On decomposition of the \( \beta \) phase:

\[ \Delta G_{\beta-\alpha} = \Delta G^\text{chem}_{\beta-\alpha} + \Delta G^\text{elastic}_{\beta-\alpha} + \Delta G^\text{plastic}_{\beta-\alpha} + \Delta G^\text{surface}_{\beta-\alpha} \]  

(2.3)

They have argued that the elastic accommodation and the surface free energies are removed by reversion of the phase, i.e.

\[ \Delta G^\text{chem}_{\beta-\alpha} = -\Delta G^\text{chem}_{\alpha-\beta} \]

\[ \Delta G^\text{elastic}_{\beta-\alpha} = -\Delta G^\text{elastic}_{\alpha-\beta} \]  

(2.4)

\[ \Delta G^\text{surface}_{\beta-\alpha} = -\Delta G^\text{surface}_{\alpha-\beta} \]

so that the thermal hysteresis reflects the total amount of plastic accommodation work done during the hydride formation and decomposition cycle. The true equilibrium solvus temperature is obtained only for unconstrained hydride i.e. in the absence of elastic and plastic accommodation terms.
Their model would suggest that neither $P_r$ or $P_d$ corresponds to equilibrium since non-equilibrium defects, i.e. dislocations, are generated along each plateau pressure branch.

Similar explanations that thermal hysteresis is due to plastic deformation have been offered for hydride precipitation in Ti-Al-H systems by Paton et al [80, 103, 104] and in Zr-H by Puls [105]. In a subsequent publication [106] Puls revised his model and proposed that the cool down terminal solid solubilities (TSS) is governed by hydride nucleation and the elastic accommodation while the heat up is dominated by plastic accommodation effect which is much smaller than that due to elastic accommodation. The heat up TSS is therefore a good approximation to the "equilibrium", or stress free, TSS and the thermal hysteresis is a reflection of the elastic accommodation energy (rather than twice the plastic work).

Lundin and Lynch [42] put forward a theory to explain hysteresis in intermetallic metal hydrides based on an atomistic model. It focuses on the effect of hydrogen atoms occluded in the interstitial sites in the metal lattice and the resulting strain imposed. The hysteresis is attributed to an effect related to the observation that the larger the interstitial hole size, the more negative the free energy of hydride formation and the lower plateau pressure [107]. In absorption the $\alpha$ and $\beta$ phases are compressively strained,
whereas in desorption they are essentially strain free. The interstitial holes, therefore, are smaller in absorption than desorption of hydrogen, resulting in higher absorption pressure and lower desorption pressure. They concluded that strain effects are the causative factor. They proposed that regardless of whether particle size is large or small, the hysteresis effects are manifested at the atomic level, and hence the particle size (or the amount of cycling) has little effect on the presence of hysteresis. They also suggested that the desorption plateau pressure is the closest approach to equilibrium conditions.

Dayan and Mintz [47] studied the \((La_{0.5}Ce_{0.5})Ni_{5-x}Co_{x}\) system and concluded that the very large hysteresis in some cerium-containing \(LaNi_5\)-type compounds-H system is due (i) to the presence of cerium atoms and (ii) to the formation of the expanded \(LaNi_5\)-type hydride.

The most comprehensive work in recent years on hysteresis in metal-hydrogen systems is that of Flanagan and coworkers [28, 55-57, 108-121]. They extended Birnbaum's [84] model for thermal hysteresis to pressure hysteresis, i.e. the origin of hysteresis is the plastic deformation during both hydride formation and hydride decomposition and the free energy loss due to hysteresis equals the total amount of plastic accommodation work done during the hydride formation and decomposition cycle. They further related this plastic model for hysteresis to Wagner's contention that hysteresis is due.
to the fact that the chemical potentials of the metal atoms are not equal in \( \alpha \) and \( \beta \) phases. They proposed that the plastic deformation is the same for both hydride formation and decomposition in metal-hydrogen systems and hence that the half-way point between \( \frac{1}{2}RT\ln P_f \) and \( \frac{1}{2}RT\ln P_d \) corresponds to the true equilibrium situation. Their argument is as follows:

Hydrogen segregates to the stress field about edge dislocations and the solubility enhancements in the dilute \( \alpha \) phase of palladium can be used as a probe for dislocation densities [122]. The increase in hysteresis solubility in a palladium sample subjected to both phase changes is about twice that found for a sample which has been subjected only to the hydride decomposition phase change [108]. Therefore, dislocation arrays of comparable densities are produced during both hydride formation and hydride decomposition in a hysteresis loop. Further cycles of phase changes in Pd-H alloys did not increase the observed solubility enhancement [123]. The hysteresis energy loss is the same, to within experimental error, for each cycle and therefore dislocations generated during each phase change must be subsequently annihilated, leaving the dislocation density at a large saturation value. After the first cycle of \( \alpha \rightarrow \beta \) and \( \beta \rightarrow \alpha \) phase changes, a further cycle returns the sample to its initial highly dislocated state. The energy expended to create the new dislocations subsequently appears as heat.
which is transferred to the surroundings. The creation of dislocations is taken to be equivalent to plastic deformation [28, 110]. Using the regular interstitial solution approximation they derived quantitative relations between the free energy loss in completing a hysteresis loop, $1/2RT \ln(P_f/P_d)$ and the energy expended to create dislocation in hydride formation or hydride decomposition, $\Delta H_{\text{disl}}$ [28]

$$1/2RT \ln(P_f/P_d) = 2\Delta H_{\text{disl}} = RT \ln(a'/a'') \tag{2.5}$$

Eq. 2.5 also gives the relation between pressure hysteresis and thermal hysteresis (refer to Fig. 2.1 for the definition of $a'$ and $a''$). In derivation of Eq. 2.5 it is assumed that the energy needed for dislocation generation in hydride formation, $\Delta H^f_{\text{disl}}$ is equal to that in hydride decomposition, $\Delta H^d_{\text{disl}}$

$$\Delta H^f_{\text{disl}} = \Delta H^d_{\text{disl}} = \Delta H_{\text{disl}} \tag{2.6}$$

Although not explicitly given in their derivation it should follow naturally from their argument that

$$1/2RT \ln(P_f/P_{eq}) = \Delta H^f_{\text{disl}} = \Delta H^d_{\text{disl}} = 1/2RT \ln(P_{eq}/P) \tag{2.7}$$

i.e. the free energy loss due to hysteresis in hydride formation equals that in hydride decomposition. Hence
\[ P_{eq} = (P_f \cdot P_d)^{1/2} \]  \hspace{1cm} (2.8)

In recent publications Flanagan et al. [118-121] agreed with McKinnon's theory (see below) that the free energy dissipation during hydride formation and decomposition causes hysteresis. They derived a more general equation for the calculation of the loss of free energy in hysteresis cycles

\[-\Delta G(\text{cycle}) = \frac{1}{2}(b-a)RT\ln(P_f/P_d) = \Delta W(\text{cycle}) \]  \hspace{1cm} (2.9)

where \( \Delta G(\text{cycle}) \) and \( \Delta W(\text{cycle}) \) are the total irreversible dissipation of free energy (free energy loss) and the net work done by the surroundings on the system in a hysteresis cycle, respectively. They admitted that while Eq. 2.8 may hold for the Pd-H system (based on the argument above) it is not possible to demonstrate from thermodynamic arguments alone that the free energy loss due to hysteresis should be equal for hydride formation and hydride decomposition, and indeed they may not be generally equal. They also extended their model to oxides [118] and high pressure metal hydrides [119].

Examination of Flanagan's argument gives rise to some questions. First, although experimental results on solubility enhancements suggest that similar amounts of dislocation densities are produced during hydride formation and hydride
decomposition in the first cycle of phase conversion, it seems no conclusion can be drawn that the same is true in further cycles. Secondly, it is incorrect to take the creation of dislocations to be equivalent to plastic deformation. Plastic deformation involves the movement of dislocations as well as the creation of dislocations. Without the movement of dislocations there would be no plastic deformation. The energy dissipation during plastic deformation results from both the movement and creation of dislocations. Since solubility enhancement experiments can only provide information about dislocation density they would not provide complete information about plastic deformation. Hence, it may not be correct to say that experimental observations of solubility enhancements in the $\alpha$ phase of PdH$_n$ proves the proposition that the plastic deformation is the same for both hydride formation and decomposition as believed by Flanagan and coworkers.

Park and Flanagan [114, 117] offered an explanation for the effect of aliquot size on hysteresis using the concept of local equilibrium at the interface which was developed by Hultgren [124], Hillert [125] and Purdy et al. [126] for interpreting phase transformation in Fe-M-C systems (M: alloying elements). The hysteresis discussed above was termed plastic hysteresis and the hysteresis related with aliquot size chemical hysteresis. They proposed that the origin of the effect of aliquot size on the hysteresis is due to the
interface velocity on the metal atom local equilibrium at the interface between the \( \alpha \) and \( \beta \) phases. Their argument is based on the assumption that complete equilibrium cannot be obtained because of the negligible movement of the metal atom components at the relative low temperatures at which most of investigations are carried out but it seems likely that local interface equilibrium may be established because metal atom diffusion in the vicinity of interface is many times more rapid than in the bulk [125]. Large aliquots of hydrogen lead to rapid initial interface velocities which can result in the destruction of metal atom pile-up (metal atom local equilibrium) at the interface. When the driving pressure during the large aliquot falls below a certain value the pile-up builds up again but does not reach the composition characteristic of small aliquots. Since the chemical potential of hydrogen is a function of the metal atom composition at the interface the hydrogen chemical potential will be lower during hydriding for the large aliquot case than for small aliquot case, resulting in chemical hysteresis. According to this explanation, there would be no effect of aliquot size on the hysteresis in pure metal-hydrogen systems.

N. Shohoji [127] agreed with Flanagan's model in qualitative aspects and proposed modifications in quantitative aspects.

Sinha and Wallace [38] do not agree with Flanagan's model
and question whether dislocation generation during hydrogenation and dehydrogenation can be considered to be primarily responsible for hysteresis. They argue that on hydrogenation, metals and alloys experience a reversible volume expansion of as much as 25% without a change of crystal structure so that an enormous amount of elastic strain energy is stored in the lattice during hydrogenation and is subsequently released during dehydrogenation. They computed the strain energy for hydrogenation of ZrMn$_{1.22}$Fe$_{1.11}$ and ZrMn$_{1.11}$Fe$_{1.22}$ using a theoretical strain energy model developed by Sinha et al. [128]. According to this model, when an impurity atom of radius $r_0$ occupies a smaller interstitial site of radius $r'$ in a parent lattice, the distortion produced around the impurity atoms are to a first approximation spherically symmetric and only normal stress and strain fields are present. The final equations are [128]

$$E_a = \frac{8\pi \mu}{9} \left( \frac{1+\nu}{1-\nu} \right)^2 \epsilon^2 r'$$ \hspace{1cm} (2.5)

$$E_a = 6 \frac{1-\nu}{1+\nu} E_m$$ \hspace{1cm} (2.6)

$$E_i = 14.4 \frac{1-\nu}{1+\nu} E_m 2 \left( \frac{r'}{d} \right)^3$$ \hspace{1cm} (2.7)

where $E_m$ is the strain energy in the matrix, $E_a$ is the strain energy stored in the impurity atom (hydrogen in the present
case), $E_i$ is the interaction energy when neighboring interstitial sites are occupied, $\mu$ is the shear modulus, $\nu$ is Poisson's ratio, $Z$ is the number of near-neighbor sites surrounding a given site, $d$ is the distance between sites and $\varepsilon = (r_0 - r')/r'$. The total energy when an impurity atom (hydrogen in the present case) occupies an interstitial site is then

$$E_a = E_m + E_a + E_i \quad (2.8)$$

By computing strain energies associated with various interstitial sites from the known crystal structure and estimated elastic constant data the weighted average strain energies were obtained which are in good agreement with the experimentally observed free energy differences in the absorption and desorption PC isotherms. From this Sinha and Wallace concluded that hysteresis is primarily a consequence of strain energy. During absorption, the hydrogen atom occupies a smaller interstitial site; thus it has to overcome a strain energy barrier, causing $P_r$ to acquire a high value. During hydride decomposition the lattice is relaxed and there is no strain energy barrier. Consequently $P_d$ is lower in magnitude. Their model also explains quite well why the $P_r/P_d$ ratio decreases with increasing temperature, acquiring a value of almost unity at high temperatures. With rising temperatures the lattice parameter increases and $\mu$ decreases.
and both of these result in decreased strain energy. However, their calculation of strain energy may be seriously in error because they did not consider the effects on strain energy of the plastic deformation and the free surface of a fine powder.

McKinnon [29] has examined the conditions of two-phase coexistence in guest-host systems like the metal hydrides, assuming that conversion between the two phases dissipates energy. He pointed out that from elementary thermodynamics we know that completing a hysteresis loop such as that in Fig. 2.1 converts work done on the sample to heat, with the work done and the heat produced being equal to the area of the hysteresis loop. Therefore, any mechanism which causes energy dissipation during phase conversion would produce hysteresis. From the second law of thermodynamics and by taking into account the irreversible behavior of energy dissipation McKinnon derived the thermodynamic relationships showing that any energy dissipation during phase conversion allows the two phases to coexist over a range of chemical potential and end phase compositions, and hence can account for hysteresis in the metal hydrides. He pointed out that the plastic deformation during phase conversion will contribute to hysteresis because of the energy dissipation. He also proposed that nucleation effects could lead to the energy dissipation and hence contribute to hysteresis. In his discussion, the internal stresses resulting from phase
conversion are assumed to be completely relaxed by plastic
deformation. This assumption, in general, seems
oversimplified.

Wicke and Blaurock [129] performed precise measurements
of PC isotherms for Pd-H and Pd-D systems. The evaluation of
the PC isotherm above the critical temperature, where no
hysteresis occurs and hence equilibrium values could be
obtained, yielded a value of the critical concentration $n_c = 0.257 \pm 0.004$ ($n$ is the atomic ratio D/Pd or H/Pd). By
evaluation of PC isotherms below the critical temperature it
was shown that the desorption branches of the hysteresis in
the two phase region lead to the same $n_c$ value, whereas the
absorption branches yield $n_c = 0.295 \pm 0.005$. On the basis of
this finding it was concluded that the desorption branches
represent the true strain-free equilibrium; the absorption
branches represent, instead, an equilibrium under mechanical
constraints. They also attributed the decreasing of plateau
pressure of absorption during the first few cycles to the
increasing dispersion of the metal.

2.2 Sloping Plateaus

2.2.1 Experimental Observations

The phase rule requires that the hydrogen pressure in
equilibrium with a metal phase and a metal hydride phase
should be invariant at a given temperature, i.e. the PC
isotherm should be horizontal in the two phase region. This
constant pressure range is usually referred to as the pressure plateau. In experimental PC isotherms, however, sloping plateaus are often observed, i.e. the hydride formation/decomposition pressures are increasing/decreasing during the phase conversion. This non-ideal behavior can be characterized by the plateau slope, \( \frac{d\ln P}{d(H/M)} \), defined as the sloping factor. Plateau slopes for some commercial hydride forming materials are listed in Table 2.6 [49].

The Effects of Sample Inhomogeneities and Annealing

Sample inhomogeneities can result in sloping plateaus. Fig. 2.7 shows the desorption PC isotherms for \( \text{LaNi}_x \) with \( x \) value ranging from 4.90 to 5.50 [130]. The plateau pressures increase from 280 Kpa for \( \text{LaNi}_{4.90} \) to 930 Kpa for \( \text{LaNi}_{5.50} \) hence a small variation of alloy composition can result in a large change of plateau pressures.

Annealing treatments prior to hydriding can reduce the slopes. Relations of annealing time and plateau slopes for \( \text{MgNi}_{4.5} \text{Al}_{0.5} \)-Hydrides are illustrated in Fig. 2.8. Plateau slopes decrease with increasing annealing time but the effect tends to saturate. Table 2.7 lists the effect of annealing on plateau slopes for a number of intermetallic compound - hydrogen systems [45, 131-133]. The annealing greatly reduces the plateau slopes but does not eliminate them. In contrast to these experimental results, Komazaki et al. [40] found no marked flattening of the plateau in either absorption or
desorption isotherms in their investigation of the effect of annealing on the FC isotherms for Ti-Zr-Fe-Mn hydrides. Sloping plateaus are also observed in some other well-annealed materials [see, e.g. Ref. 37, 135-139]. There seems to be an optimum annealing condition. Annealing at too high temperatures will not only cause a severe loss of capacity but also increase plateau slopes (Fig. 2.9) [131].

The Effect of Temperature

Plateau slopes at various temperatures for various hydride forming materials are listed in Table 2.8 [35, 37, 39, 131]. In contrast to hysteresis phenomenon, there seems to be no general tendency of the effect of temperature on plateau slopes. The plateau slopes are almost constant for hydride formation and, to a lesser degree, for hydride decomposition in PrNi₅-H system over a small temperature range (293-323). While there is no complete data for hydride formation of MnNi₄.5Al₀.5 (annealed at 1125°C for 4 hours) plateau slopes for hydride decomposition decrease with increasing temperature. The experimental data in ZrMn₂-H system were obtained after annealing the starting material at 800-900°C for a week. The plateau slopes decrease slightly with increasing temperature for hydride decomposition but the same tendency is not observed for hydride formation. In a large temperature range from 293K to 673K the absorption plateau slopes in Zr(Fe₀.₃Mn₀.₇)₂ hydride decrease with
increasing temperature up to 573K and then rise again, whereas there seems no temperature dependence of desorption plateau slopes.

Also listed in Table 2.8 are values of the differential of the free energy during phase conversion with respect to hydrogen content, \( \frac{d(1/2RT\ln P)}{d(H/M)} \). These values are more constant than those calculated from \( \frac{d\ln P}{d(H/M)} \). The expression \( \frac{d(1/2RT\ln P)}{d(H/M)} \) may be the better representation of the characteristics of the sloping plateau behavior.

The Effect of Alloy Composition

Alloy composition may greatly affect the plateau slopes (Table 2.9) [45, 131]. In general, the sloping plateau phenomenon is more pronounced in intermetallic compounds, especially when the intermetallic compounds are multicomponent or non-stoichiometric whereas in pure metal-hydrogen systems the $\gamma$-PC isotherms in the two phase region are often horizontal, or nearly so. The partial elemental substitution, which provides a means of altering hydrogen absorption and desorption characteristics to meet specific application requirements, often results in the increasing plateau slopes. The substitution of Al for Ni in MnNi$_{5-x}$Al$_x$ greatly increases plateau slopes [45]. The plateau slopes increase from 0.22 to 1.55 for hydride formation and from 0.13 to 1.43 for hydride decomposition when $x$ value
increases from 0 to 0.5. The desorption plateau slopes in CaMnNi₅₋ₓH systems change dramatically with the variation of x value (Fig. 2.10) [131]. The desorption plateau slope for MnNi₅₋ₓH (x=0) at 298K is 0.34. With the substitution of Ca for Mn the slope remains nearly constant in the x value range of 0 to 0.2 then increases sharply to reach a maximum slope of 3.62 at x=0.7. The further increase of x value reduces the slope rapidly with the slope being 0.19 for CaNi₅₋ₓH (x=1).

Experimental observations have also been reported where the hydride of multicomponent intermetallic compounds show very small plateau slopes and pure metal-hydrogen systems exhibit pronounced sloping plateaus. Flat plateaus were observed in desorption PC isotherms for the Ce₀.₅La₀.₅Ni₂.₅Cu₂₅₋ₓH and Ce₀.₈Pr₀.₂Ni₂.₅Cu₂₅₋ₓH systems [140], and for the Zr₀.₇Ti₀.₃Mn-H system [141]. In the Pa-H system [77], multiple plateaus are observed with the formation of three hydrides. While the plateaus corresponding to the equilibrium between the solid solution and hydride I are horizontal the remaining plateaus which correspond to the equilibrium between hydrides show pronounced slopes. Similar results have been observed in Sm-H [32] and Pu-H [142] systems.

The Effect of Absorption and Desorption Cycling

It has been observed that in LaNi₅₋ₓH system the
absorption plateau slope can be reduced during the first few cycles whereas the desorption plateau slope remains almost constant [58]. Plateau slope changes have also been observed in long term cycling experiments. Goodell [63] reported a marked increase of the plateau slopes after 1500 absorption and desorption cycles of LaNi$_5$. In his experiment, the absorption and desorption of hydrogen was induced by the change of hydrogen pressure and fresh hydrogen was used for each cycle. Kim and Lee [67] observed only slight increase of the plateau slopes for MnNi$_{4.5}$Al$_{0.5}$ and MnNi$_{4.15}$Fe$_{0.85}$ hydrides after 3000 thermal cycles where hydrogen absorption and desorption was induced by the change of sample temperature in a closed reactor.

2.2.2 Theoretical Explanations

In contrast to hysteresis, not many theoretical explanations for sloping plateaus in metal-hydrogen systems have been proposed in the literature, although both phenomenon are widely observed experimentally and of importance in the application of metal hydrides.

In their model for the hysteresis in the Pd-H system Scholtus and Hall [100] also related the sloping plateau to the stress effect. The volume increase accompanying the $\alpha$ to $\beta$ transition must take place against the internal pressure required to expand the metal. The latter increases with extension (the amount absorbed) until the yield limit of the
metal is reached; ideally it would then remain constant while the \( \alpha \) phase is converted into the \( \beta \) phase. However, since the yield strength varies from point to point throughout the metal, absorption does not ordinarily take place at a sharply defined transition pressure, i.e. a series of compositions exist corresponding to different (increasing) hydrogen pressures.

Oesterreicher [143, 144] proposed that inhomogeneities and above critical behavior can result in the sloping plateaus in PC isotherms. His argument is based on a local environmental model which was developed by Jacob and coworkers [145, 146]. According to this model the number of H atoms taken up is assumed to be dictated by the special local environments, the number of which is given by binomial distribution functions. Oesterreicher took an alternate approach by assuming characteristic hydrogen pressures at which local interaction configurations became filled. This results in steps in the PC isotherms which when taken on sufficiently large clusters and further smoothed out appear similar to above critical behavior.

Oates and Flanagan [147] presented an explanation for sloping plateaus in terms of local equilibrium at the interface [124-126]. It was argued that the local interfacial equilibrium in hydride formation would result in an increase of hydrogen concentration in both bulk phases, i.e. the solid solution and hydride phase, as the amount of hydride phase is
increased. The hydrogen potential, therefore, increases with increasing absorption, leading to sloping plateaus. This explanation has problems because of the misinterpretation of the local equilibrium model. In a recent communication Flanagan [148] agreed with the author that their explanation for sloping plateaus is probably incorrect.

Ivey and Northwood [149] observed by the X-ray diffraction method that the hydride composition in $\text{Zr(Fe,Cr}_{1-x})_2$ (x=0.25, 0.45) intermetallics increases slightly through the two-phase region as hydrogen levels in the compounds increase. They suggested that this phenomenon may be related to the sloping plateau behavior of these intermetallic compound-hydrogen systems, as the variable hydrogen composition presents an additional degree of freedom.

Matsumoto and Matsushita [150] proposed that the sloping plateaus in $\text{LaNi}_5 - H$ system can be interpreted in terms of the formation of some intermediate phases which have slightly different equilibrium pressure. The slope may be caused by the occurrence of a small step on the plateau of the PC isotherm. Using in situ X-ray analysis they observed a metastable hydride phase with an estimated composition close to $\text{LaNi}_5H_4$. They suggested that this metastable phase forms around the $\alpha/\beta$ interface and is induced by the strains caused by phase transformation.
### Table 2.1 Experimental Observations of the Effect of Temperature on Hysteresis

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<td>Tl$<em>{0.5}$Cr$</em>{0.5}$Mn$<em>{0.8}$Fe$</em>{2.17}$</td>
<td>373</td>
<td>442</td>
<td>337</td>
<td>1.31</td>
<td>0.42</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>393</td>
<td>802</td>
<td>629</td>
<td>1.28</td>
<td>0.40</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>413</td>
<td>1340</td>
<td>1150</td>
<td>1.17</td>
<td>0.27</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>433</td>
<td>2230</td>
<td>1940</td>
<td>1.15</td>
<td>0.25</td>
<td>[40]</td>
</tr>
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</table>

* at the midpoint of the plateau pressures
Table 2.2 Experimental Observations of the Effect of Alloy Composition on Hysteresis in Alloy-Hydrogen Systems

<table>
<thead>
<tr>
<th>Materials</th>
<th>X</th>
<th>P_f (kPa)</th>
<th>P_d (kPa)</th>
<th>P_f/P_d</th>
<th>1/2RTlnP_f/P_d</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>V Nb_x (1-x)</td>
<td>1.0</td>
<td>876</td>
<td>398</td>
<td>2.2</td>
<td>1.03</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>1621</td>
<td>73</td>
<td>22.2</td>
<td>4.03</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td>Zr(Fe_{x}Cr_{1-x})_{2}</td>
<td>0.45</td>
<td>23.1</td>
<td>13.4</td>
<td>1.72</td>
<td>0.66</td>
<td>[26]</td>
</tr>
<tr>
<td>(293K)</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td></td>
<td></td>
<td></td>
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<td>[26]</td>
</tr>
<tr>
<td>LaNi_x (Fe_{x})_{1-x}</td>
<td>0.0</td>
<td>220</td>
<td>172</td>
<td>1.28</td>
<td>0.30</td>
<td>[48]</td>
</tr>
<tr>
<td>(298K)</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>145</td>
<td>105</td>
<td>1.38</td>
<td>0.40</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>68</td>
<td>55</td>
<td>1.24</td>
<td>0.26</td>
<td>[48]</td>
</tr>
<tr>
<td>(La_{0.5}Ce_{0.5})CoNi_{x}</td>
<td>0.2</td>
<td>3240</td>
<td>1510</td>
<td>2.15</td>
<td>0.95</td>
<td>[47]</td>
</tr>
<tr>
<td>(298K)</td>
<td>0.5</td>
<td>2130</td>
<td>1400</td>
<td>1.52</td>
<td>0.52</td>
<td>[47]</td>
</tr>
<tr>
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<td>1.0</td>
<td>1580</td>
<td>1500</td>
<td>1.05</td>
<td>0.06</td>
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</tr>
<tr>
<td></td>
<td>2.0</td>
<td>476</td>
<td>446</td>
<td>1.07</td>
<td>0.08</td>
<td>[47]</td>
</tr>
<tr>
<td>CaMn_x (Ni_{1-x})_5</td>
<td>0.0</td>
<td>12000</td>
<td>2330</td>
<td>5.15</td>
<td>2.03</td>
<td>[49]</td>
</tr>
<tr>
<td>(298K)</td>
<td>0.2</td>
<td>3750</td>
<td>2530</td>
<td>1.48</td>
<td>0.49</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>425</td>
<td>385</td>
<td>1.10</td>
<td>0.12</td>
<td>[49]</td>
</tr>
</tbody>
</table>

* at the midpoint of plateau pressures
<table>
<thead>
<tr>
<th>Materials (Temperature)</th>
<th>X</th>
<th>$P_r$ (kPa)</th>
<th>$P_d$ (KPa)</th>
<th>$P_r/P_d$</th>
<th>$1/2RTlnP_r/P_d$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_{1-x}$CrMn</td>
<td>0.0</td>
<td>3.00</td>
<td>1.20</td>
<td></td>
<td></td>
<td>[50]</td>
</tr>
<tr>
<td>(263K)</td>
<td>0.2</td>
<td>1.15</td>
<td>0.15</td>
<td></td>
<td></td>
<td>[50]</td>
</tr>
<tr>
<td>Ti$<em>{1-x}$Cr$</em>{1.2}$Mn$_{0.8}$ (263K)</td>
<td>0.1</td>
<td>1.15</td>
<td>0.15</td>
<td></td>
<td></td>
<td>[50]</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>1.05</td>
<td>0.05</td>
<td></td>
<td></td>
<td>[50]</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>1.02</td>
<td>0.02</td>
<td></td>
<td></td>
<td>[50]</td>
</tr>
<tr>
<td>MnNi$_{5-x}$Al$_x$ (313K)</td>
<td>0.0</td>
<td>2.38</td>
<td>1.13</td>
<td></td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.96</td>
<td>0.88</td>
<td></td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>1.68</td>
<td>0.67</td>
<td></td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>1.45</td>
<td>0.48</td>
<td></td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>1.27</td>
<td>0.31</td>
<td></td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.26</td>
<td>0.30</td>
<td></td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$ (303K)</td>
<td>1.57</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.4}$ (303K)</td>
<td>1.24</td>
<td>0.27</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$B (303K)</td>
<td>1.44</td>
<td>0.46</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$Co (303K)</td>
<td>1.25</td>
<td>0.28</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$Cr (303K)</td>
<td>1.32</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$Cu (303K)</td>
<td>1.42</td>
<td>0.44</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$Mo (303K)</td>
<td>1.42</td>
<td>0.44</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$Nb (303K)</td>
<td>1.28</td>
<td>0.31</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$Si (303K)</td>
<td>1.31</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$Ti (303K)</td>
<td>1.33</td>
<td>0.36</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$V (303K)</td>
<td>1.31</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$V (303K)</td>
<td>1.41</td>
<td>0.43</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>MnNi$<em>{4.7}$Al$</em>{0.3}$Zr (303K)</td>
<td>1.08</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
</tbody>
</table>

* at the midpoint of plateau pressures

54
Table 2.3 The Effect of Aliquot Size on Hysteresis [56]

<table>
<thead>
<tr>
<th>System</th>
<th>T (K)</th>
<th>$1/2RT\ln\left(\frac{P_r^s}{P_d^s}\right)$</th>
<th>$1/2RT\ln\left(\frac{P_r^1}{P_d^1}\right)$</th>
<th>$1/2RT\ln\left(\frac{P_r^s}{P_r^1}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi$_5$-H</td>
<td>298</td>
<td>630</td>
<td>300</td>
<td>164</td>
</tr>
<tr>
<td>LaCo$_5$-H</td>
<td>323</td>
<td>370</td>
<td>195</td>
<td>87</td>
</tr>
<tr>
<td>ZrMn$_2$-H</td>
<td>348</td>
<td>2790</td>
<td>2390</td>
<td>200</td>
</tr>
</tbody>
</table>

* estimated value
<table>
<thead>
<tr>
<th>Variable</th>
<th>Effect on Hysteresis</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Generally decreasing with increasing temperature</td>
<td>[30-40]</td>
</tr>
<tr>
<td>Alloy Composition</td>
<td>May depend dramatically on alloy composition</td>
<td>[26,45-51]</td>
</tr>
<tr>
<td>Hydrogen Aliquot Size</td>
<td>Decreasing with increasing aliquot size to a limiting value</td>
<td>[54-56]</td>
</tr>
<tr>
<td>Annealing of Metal Sample</td>
<td>Increasing with increasing annealing temperature for LaNi$_5$ but no significant change for LaCo$_5$</td>
<td>[57-59]</td>
</tr>
<tr>
<td>Absorption/Desorption</td>
<td>Decreasing with increasing amount of cycling during first few cycles and then remaining constant</td>
<td>[34,43,58,60,61]</td>
</tr>
<tr>
<td>Cycling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle Size</td>
<td>Large for bulk sample than for finely divided sample</td>
<td>[34,43,73]</td>
</tr>
</tbody>
</table>

Table 2.4 Summary Table Showing Effect of Different Variables on Hysteresis
<table>
<thead>
<tr>
<th>Author</th>
<th>System</th>
<th>Origin of Hysteresis</th>
<th>Position of $P_{eq}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ubbelohde</td>
<td>Pd-H</td>
<td>Hydride is strained</td>
<td>$P_d$</td>
<td>[92]</td>
</tr>
<tr>
<td>Lacher</td>
<td>Pd-H</td>
<td>Oversaturation of the phase on absorption and undersaturation of the phase on desorption</td>
<td>Midpoint of $P_r$ and $P_d$</td>
<td>[94]</td>
</tr>
<tr>
<td>Wagner</td>
<td>Pd-H</td>
<td>$\mu^a_x = \mu^b_x$</td>
<td></td>
<td>[95]</td>
</tr>
<tr>
<td>Libowitz</td>
<td>ZrNi-H</td>
<td>Formation of metastable hydride</td>
<td>$P_d$</td>
<td>[96]</td>
</tr>
<tr>
<td>et al.</td>
<td></td>
<td>Size of crystallites</td>
<td></td>
<td>[97,98]</td>
</tr>
<tr>
<td>Flotow</td>
<td>U-H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>et al.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Everett</td>
<td>Pd-H</td>
<td>Large volume change accompanying the transition</td>
<td></td>
<td>[99]</td>
</tr>
<tr>
<td>&amp; Nordon</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scholtus</td>
<td>Pd-H</td>
<td>Growth of hydride under compressive stress</td>
<td>$P_d$</td>
<td>[100]</td>
</tr>
<tr>
<td>&amp; Hall</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Birnbaum</td>
<td>Nb-H</td>
<td>Plastic deformation during both hydride formation and decomposition</td>
<td>Neither $P_r$</td>
<td>[84,101,102]</td>
</tr>
<tr>
<td>et al.</td>
<td></td>
<td></td>
<td>Nor $P_d$</td>
<td></td>
</tr>
<tr>
<td>Lundin</td>
<td>Intermetallic</td>
<td>Strain effect</td>
<td>Close to $P_d$</td>
<td>[42]</td>
</tr>
<tr>
<td>&amp; Lynch</td>
<td>Metal-H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flanagan</td>
<td>Metal</td>
<td>Dislocation generation during both hydride formation and decomposition</td>
<td>$(P_f \cdot P_d)^{1/2}$</td>
<td>[28,55,56,57,108-121]</td>
</tr>
<tr>
<td>et al.</td>
<td>Hydride-H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sinha &amp;</td>
<td>Metal</td>
<td>Elastic strain energy</td>
<td>$P_d$</td>
<td>[38]</td>
</tr>
<tr>
<td>Wallace</td>
<td>Hydride-H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mckinnon</td>
<td>Metal</td>
<td>Energy dissipation during phase conversion</td>
<td>Between $P_r$ and $P_d$</td>
<td>[29]</td>
</tr>
<tr>
<td>Hydride-H</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wicke &amp;</td>
<td>Pd-H</td>
<td>Strain effect</td>
<td>$P_d$</td>
<td>[129]</td>
</tr>
<tr>
<td>Blaurock</td>
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</tr>
<tr>
<td>Material</td>
<td>Temp. (K)</td>
<td>dlnP/d(H/M) *</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-----------</td>
<td>--------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaNi₅</td>
<td>298</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaNi₄.7Al₀.₃</td>
<td>298</td>
<td>0.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaNi₅</td>
<td>298</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnNi₅</td>
<td>298</td>
<td>0.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeTi</td>
<td>303</td>
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<td></td>
</tr>
<tr>
<td>Fe₀.₉Mn₀.₁Ti</td>
<td>313</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₀.₉Ni₀.₂Ti</td>
<td>343</td>
<td>0.36</td>
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<tr>
<td>Mg₂Ni</td>
<td>571</td>
<td>0.02</td>
<td></td>
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<tr>
<td>Mg₂Cu</td>
<td>597</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* principal plateau
Table 2.7 The Effect of Annealing on Plateau Slopes

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. (K)</th>
<th>$\frac{d\ln P_d}{d(H/M)}$</th>
<th>Annealing condition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ca}<em>{0.73}\text{Mn}</em>{0.3}\text{N}_{1.5}$</td>
<td>298</td>
<td>2.52</td>
<td>24 h at 1100°C</td>
<td>[131]</td>
</tr>
<tr>
<td>$\text{MnN}<em>{1.4}\text{Al}</em>{0.5}$</td>
<td>298</td>
<td>1.37</td>
<td>4 h at 1125°C</td>
<td>[131]</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>1.43</td>
<td>10 h at 1000°C</td>
<td>[45]</td>
</tr>
<tr>
<td>$\text{TiW}_{1.5}$</td>
<td>293</td>
<td>1.93</td>
<td>20 h at 1100°C</td>
<td>[132]</td>
</tr>
<tr>
<td>$\text{Tl}<em>{0.96}\text{Zr}</em>{0.04}\text{Fe}<em>{0.945}\text{Nb}</em>{0.04}$</td>
<td>303</td>
<td>0.81</td>
<td>20 h at 1000°C</td>
<td>[133]</td>
</tr>
</tbody>
</table>

59
Table 2.8 The Effect of Temperature on Plateau Slopes

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. (K)</th>
<th>$d\ln P/d(\text{H/M})$</th>
<th>$d(1/2RT\ln P)/d(\text{H/M})$</th>
<th>Ref.</th>
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<td>1.12</td>
<td>3.13</td>
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* annealed at 1125°C for 4 hours  ** annealed at 800-900°C for a week
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<th>dlnP_d/d(H/M)</th>
<th>Ref.</th>
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<td>[131]</td>
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61
Fig. 2.1 Schematic illustration of hysteresis in a metal hydrogen-system. Pressure hysteresis: \( P_f > P_d \); solvus hysteresis: \( a' > a'' \); thermal hysteresis: \( T_1 > T_2 \).
Fig. 2.2 Temperature dependence of hysteresis for $\text{MnNi}_{5-x}\text{Al}_x$ hydrides at various Al-contents [45].
Fig. 2.3 Effect of aliquot size on hysteresis in LaNi$_5$-H system [55].
Fig. 2.4 Values of $P_r^{1/2}$ at 298K for LaNi$_5$-H system plotted as a function of the annealing temperature (annealing time set at 12h) [57].
Fig. 2.5 PC isotherms for LaNi$_5$ at 298K: ○, absorption data for well-annealed activated LaNi$_5$; ▲, subsequent desorption data; □, absorption data for unannealed activated LaNi$_5$; △, desorption data for same unannealed sample [57].
Fig. 2.6 PC isotherms for LaNi$_5$ at 353K: curves AA', first cycling; curves BB', second cycling; curves CC' third cycling [58].
Fig. 2.7 Desorption PC isotherms at 40°C for LaNi$_x$ – H system (x=4.90, 5.00, 5.14, 5.25, 5.30 and 5.50) [130] showing that small variations of the alloy composition can result in large changes of plateau pressures.
Fig. 2.8 Relations of annealing time and plateau slopes for $\text{Mn}_{4.5}\text{Ni}_{0.5}\text{Al}$-hydrides at 313.2K [45].
Fig. 2.9 Effect of annealing (24 hours) on the 25°C desorption isotherms of Ca_{0.7} Mn_{0.3} Ni_{5} \[131]\.
Fig. 2.10 Variation of desorption plateau slopes (calculated from data in Ref. 131) in Ca\textsubscript{M}M\textsubscript{1-x}Ni\textsubscript{x} (x=0-1.0) hydride at 298K with x value.
CHAPTER 3
EXPERIMENTAL DETAILS

3.1 Materials

The Zr alloy samples used in this investigation were prepared from 99.9% pure zirconium, 99.9% pure iron and 99.999% pure chromium. The starting materials were cleaned by soaking in an agitated bath of acetone followed by washing with ethanol. The constituents were weighed to ± 1 mg on a microbalance prior to melting.

Two sets of samples of the same composition were prepared. One set was cast in a vacuum arc furnace in our laboratory at the University of Windsor. The arc furnace unit was partly reconstructed for better vacuum and for efficient and safe operation. A stainless steel cylinder with two observing windows replaced the quartz cylinder. A new copper hearth was machined which can accommodate two samples and a getter material. Both the thoriated-tungsten tipped electrode and copper hearth were water cooled and enclosed in the stainless steel cylinder. Ultrahigh-purity argon was used as the arcing gas at a pressure of 60 to 110 Kpa. The argon gas can also reduce the sample evaporation during melting. The current was adjusted until a molten pool of metal was obtained, typically of the order of 100 A. Argon was introduced into the arc furnace after the evacuation and the
atmosphere was further purified by melting the zirconium getter. After the first melting the ingots were turned over and remelted. This operation was repeated several times to ensure homogeneity. Typical sample weights were about 20 grams.

The other set was cast by induction melting in a water-cooled copper boat under a titanium-gettered flowing argon atmosphere at the University of Pittsburgh. Each sample (about 4 grams) was melted 4-5 times with being turned over prior to each melting, and was held in the liquid state for about 30 seconds to ensure complete mixing of the starting materials. Both sets of samples were vacuum annealed for 24 hours at 1000°C.

Quantitative chemical analysis of the composition of the samples prepared by arc melting was performed at Teledyne Wah Chang Company, Albany, Oregon and the results are listed in Table 3.1. Better agreement between the attempted and analyzed compositions and lower oxygen levels were obtained than those in a previous investigation [151].

Commercial LaNi₅ was purchased from Ergenics Corporation and was vacuum annealed for 24 hours at 1100°C. Calibration grade hydrogen was supplied by Liquid Carbonic Inc. with purity of 99.999% and impurities being 1 ppm O₂, 1 ppm N₂, <0.5 ppm CH₄ and <1 ppm H₂O.
3.2 Pressure-Composition (PC) Isotherm Measurement

3.2.1 Apparatus

A Sieverts'-type apparatus was developed for this investigation. A schematic diagram of the apparatus is shown in Fig.3.1. The apparatus must have perfect seals at both high hydrogen pressure and high vacuum. This is one of the major difficulties in constructing the apparatus. Any small leak would lead to errors in the determination of the amount of hydrogen absorbed or desorbed by the sample and hence affect the accuracy of PC isotherms. A leak would also cause contamination of the sample. Great care was taken in the design and installation of the apparatus to eliminate any leaks. The whole system is made of stainless steel. The connections are as few as possible. Type 304 stainless steel Swagelok or threaded fittings were utilized for all connections. Threaded joints were sealed by wrapping with teflon tape. All valves are of the stainless steel bellows type which eliminate any leaks from the operation of valves. Even so, there were small leaks after the completion of the installation of the apparatus. Much time was spent on the leak "hunting" until a "leak-free" system was obtained such that charging the apparatus to 30 atm hydrogen, which is about three times higher than the usual working hydrogen pressure, the pressure had remained unchanged for more than two weeks.

The main section of the apparatus consists of the reactor
system (Fig.3.2). The reactor vessel was machined from a type 304 stainless steel bar, with two tapped ports for inlet or outlet gas and thermocouple connections respectively. An O-ring sealed end-plate, fastened with four stainless bolts, provides a good seal and facilitates loading and removal of alloy specimens. A sintered stainless steel filter with 0.5μm pore diameter is used to prevent the escape of the very fine sample powder (the mean size of which is about 10 μm). Two filling bars made of aluminum are placed into the reactor to reduce its volume. The reactor volume with the filling bars was carefully calibrated as 31.5±0.3 ml. A small reactor volume is required to maximize the pressure change resulting from the absorption or desorption of hydrogen by a certain amount of sample. A shielded K-type thermocouple is sealed into the reactor and its tip is located in the center of sample powder, thus eliminating errors arising from the temperature difference between the thermocouple and the sample if the thermocouple were not inserted in sample powder, and enabling the thermocouple to monitor the sudden change of the sample temperature upon hydrogen absorption or desorption with a fast time response.

The reactor is immersed in a thermostatted water bath which allows the temperature to be controlled to within 0.1K. The bath is vigorously stirred to optimize heat transfer. The whole reactor volume including the connecting tube is kept in the water bath so that there is no temperature gradient built
up in the reactor and the accuracy of the measurement of the equilibrium pressure will not be affected by the change of the differences between the reactor temperature and the ambient temperature.

The pressure is measured by pressure transducers and recorded using a chart recorder. Three pressure transducers are used to improve the experimental accuracy. These transducers have pressure measurement ranges 0-50 psi absolute, 0-150 psi absolute, and 0-500 psi gauge. Accuracy is 0.5% of full scale. Combined with a small reactor volume, these pressure transducers make it possible to measure PC isotherms from samples as small as 2g with the desired accuracy.

A hydrogen cylinder and an argon cylinder are connected to the reactor through a valve and a pressure regulator. The argon gas is ultra high purity (UHP) grade and used for bleeding purpose. A mechanical/diffusion type vacuum pump is also connected to the reactor. Check valves are installed at key positions in the apparatus to ensure unidirectional flow. Relief valves, connected to all pressure transducers, provide a means of relieving accidental overpressures.

3.2.2 Procedure

An annealed bulk sample is crushed in a pestle and mortar. Because of the brittle nature of these intermetallics, this is achieved with little difficulty.
Particle size is variable, generally less than 1 mm. The crushed sample is weighed on a microbalance to ± 1 mg and then placed in the sample chamber of the reactor. The sample size is typically about 3 grams. The reactor system is evacuated to a residual pressure of $10^{-5}$ torr and then bled with ultra-high pure grade argon gas. This procedure is repeated several times for a period of four hours, until final evacuation. Hydrogen is then admitted into the reactor at pressures above the equilibrium pressure. In most cases, hydrogen is absorbed within a few minutes, without any further activation treatment.

PC isotherms of hydrogen absorption and desorption for $\text{Zr(Fe}_{x}\text{Cr}_{1-x})_2$ ($x = 0.5, 0.6, 0.7, 0.8$) are determined both for the first three cycles of hydride formation and decomposition at 302.2 K and for well activated samples (after cycling through the phase conversion 5 times) at various temperatures. The amount of hydrogen absorbed or desorbed is calculated from the pressure change in the constant volume. Since hydrogen behaves very nearly like an ideal gas at temperatures ( < 100°C ) and pressures ( < 4000 Kpa ) of interest in this study, the ideal gas law is used. The results are expressed as plots of the hydrogen absorption and desorption pressure vs. hydrogen to metal ratio (H/M) of the sample.

Absorption isotherm measurements are started with a virgin sample or a completely desorbed sample. An aliquot
(dose) of hydrogen is introduced into the reactor. The pressure change is measured by the pressure transducer and recorded in the chart recorder. Most of hydrogen is absorbed within 10 minutes and typically after 20 minutes no further pressure change can be detected. However, two hours are allowed for equilibrium pressure to be obtained. Additional aliquots are then added and the same procedure repeated. Desorption isotherms are obtained by essentially reversing the absorption isotherm procedure. Fully hydrided samples are gradually dehydrided by releasing aliquots of hydrogen gas from the reactor. Again the system is allowed to equilibrate for two hours for each data point. During both absorption and desorption PC isotherm measurements, some data points correspond to long periods of equilibration (12 hours) which show no further pressure changes.

3.3 X-Ray Diffraction Line Profile Analysis

Lattice strains induced by hydride formation and decomposition were studied for Zr(Fe_{0.75}Cr_{0.25}) intermetallics by X-ray diffraction line profile analysis. A Philips PW1078 X-ray diffractometer with a goniometer and a proportional counter detection head was used to measure the diffraction line profiles. A graphite monochromator was mounted on the detector arm. CuKα radiation at 40KV and 20mA was utilized as the diffracting medium, along with a chart recorder to display the diffraction intensity, I, vs. the
Bragg angle, $\theta$. Line profiles of four $\text{Zr(Fe}_{0.75}\text{Cr}_{0.25})_2$ samples were recorded. Sample 1 is the annealed bulk sample; sample 2 mechanically crushed powder before hydriding; sample 3 and 4 are the dehydrided powders which had been subjected to one cycle and five cycles of hydriding and dehydriding, respectively. Fast scan [$2^\circ(2\theta)/\text{min}$] was first used to identify the peaks to be analyzed and then slow scan [$0.125^\circ(2\theta)/\text{min}$] was performed over the selected peaks. Care was taken to record the intensity for a considerable distance on either side of the diffraction line in order to ensure the correct background was attained.

Several methods of obtaining crystal size and microstrains separately from X-ray powder diffraction line profile analysis have been developed [152, 153]. In the present investigation the integral breadth methods were employed. The breadth $\beta$ of a diffraction line is defined as the integrated area between the line contour and the background divided by the maximum height:

$$\beta = \frac{\text{Total Area of Maximum}}{\text{Peak Height}} = \frac{A}{H} \text{ (rads)}^2 \tag{3.1}$$

Separation of the $K_{\alpha_1}$ and $K_{\alpha_2}$ contributions to the profile was achieved by the graphical method of Dumond - Rachinger (Appendix A) [153, 154]. The area of the resolved peaks was then obtained from the area under the total curve.
(2/3 for $\alpha_1$ component and 1/3 for $\alpha_2$ component).

After the determination of the total integral breadths, $\beta_T$, the next step is to separate the integral breadths due to the instrumental aberrations, $\beta_I$, and those from the specimens, $\beta_S$. This was carried out by applying the empirical equation developed by Wagner and Aqua [155]

$$\left(\beta_T^*\right)^2 = \beta_S^* \beta_T^* + \left(\beta_I^*\right)^2 \quad (3.2)$$

$$\beta^* = \frac{\beta \cos \theta_0}{\lambda} \quad (3.3)$$

where $\theta_0$ is the Bragg angle of the reflection and $\lambda$ the wavelength of X-ray radiation.

The line profile of sample 1 (annealed bulk sample) is assumed to be broadened only by instrumental effects and hence the line breadths of sample 1 is taken as those due to instrumental broadening for other samples. Thus from Eq. 3.2 we have

$$\beta^*_S = \frac{(\beta_T^*)^2 - (\beta_I^*)^2}{\beta_T^*} \quad (3.4)$$

The final step is to separate the contributions to the broadening from crystallite size $D$ and microstrains $\varepsilon$. This was performed by both the Wagner and Aqua [155] method.
\[(\beta_s^*)^2 = (\beta_d^*)^2 + (\beta_c^*)^2 = (1/D)^2 + 4\varepsilon^2 (d^*)^2 \quad (3.5)\]

and the Halder and Wagner [156] method

\[(\beta_s^*)^2 = (\beta_c^*)^2 + \beta_d^* \beta_s^* = 4\varepsilon^2 (d^*)^2 + (1/D) \beta_s^* \quad (3.6)\]

in both Eq. (3.5) and Eq. (3.6) \(d^* = 2\sin\theta/\lambda\), \(\varepsilon = \Delta d/2d\) and \(d\) is Bragg plane spacing. Therefore, a graph of \((\beta_s^*)^2\) against \((d^*)^2\) will give a straight line of slope \(4\varepsilon^2\) and intercept \((1/D)^2\) by Wagner and Aqua method and the plots of \(\beta_s^*\) against \((d^*)^2/\beta_s^*\) will give slope \(4\varepsilon^2\) and intercept \(1/D\) by Halder and Wagner method.

3.4 Particle Size Measurements

Particle size measurements were made of the same powder samples which are analyzed by X-ray diffraction. Each powder was dispersed on the sample holder and then coated with aluminum to make the entire sample and holder electrically conducting. A series of micrographs were taken in the SEMCO Nanalab 7 Scanning Electron Microscope with the accelerating voltage set at 15 KV. Particle sizes were determined directly from the negatives using the Ladd graphic data image analyzer.
which consists of a Rockwell AIM 65 microcomputer and a E-241 orthoplex XY coordinate sensor. More than two hundred particles were analyzed for each sample. The variable geometry of the powders made average size measurements difficult, hence the longest lengths of particles were taken as the measurement of the size. Printed results were obtained from the Rockwell AIM 65 microcomputer for the total number of particles measured, the mean particle length with its standard deviation and the histogram distribution of particle size.
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<th>Analytical Results</th>
<th>Oxygen Content (pm)</th>
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<tr>
<td>Zr(Fe(<em>{0.6})Cr(</em>{0.4})(_2))</td>
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<td>Zr(Fe(<em>{0.7})Cr(</em>{0.3})(_2))</td>
<td>Zr(Fe(<em>{0.71})Cr(</em>{0.29})(_2))</td>
<td>710</td>
</tr>
<tr>
<td>Zr(Fe(<em>{0.75})Cr(</em>{0.25})(_2))</td>
<td>Zr(Fe(<em>{0.74})Cr(</em>{0.26})(_2))</td>
<td>740</td>
</tr>
<tr>
<td>Zr(Fe(<em>{0.8})Cr(</em>{0.2})(_2))</td>
<td>Zr(Fe(<em>{0.76})Cr(</em>{0.24})(_2))</td>
<td>600</td>
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$V_1-V_8$: Valves
$PT_1, PT_2$: Pressure Transducer

Fig. 3.1 Schematic diagram of the experimental apparatus.
Fig. 3.2 Schematic illustration of the reactor system.
CHAPTER 4
EXPERIMENTAL RESULTS AND DISCUSSION

4.1 PC Isotherms and Thermodynamic Parameters

PC isotherms of hydrogen absorption and desorption are shown in Figs. 4.1 to 4.4 for Zr(Fe, Cr)\(_{1-x}\) (x = 0.5, 0.6, 0.7, 0.8) which had been cycled through the phase conversion 5 times prior to the measurements. Substitution of Fe for Cr raises the two-phase plateau pressures, with both the plateau pressures for hydride formation and decomposition for Zr(Fe, Cr)\(_{0.8, 0.2}\) being about 50 times larger than those for Zr(Fe, Cr)\(_{0.5, 0.5}\) at the hydrogen to metal ratio (H/M) = 0.5 and 303.2K.

The thermodynamic parameters for the two condensed phase co-existence regions, i.e., the enthalpy, \(\Delta H\), and the entropy, \(\Delta S\), of hydride formation and decomposition were computed using the least-squares method from the van’t Hoff plots of \(\ln P_2\) vs. \(1/T\) at various hydrogen concentrations. In all cases good linear fits to the data were observed. The results are given in Table 4.1 and 4.2, with the values of H/M at which \(P_2\) was measured. It can be seen from Table 4.1 and 4.2 that \(|\Delta H|\) decreases with increase of Fe substitution for Cr and \(|\Delta S|\) is virtually constant.

The enthalpy of hydride formation, \(\Delta H_f\), and the enthalpy
of hydride decomposition, \( \Delta H_d \) are not equal in magnitude due to hysteresis. The true equilibrium enthalpy, i.e., that without hysteresis, of hydride formation, \( \Delta H_{f,eq} \), or the true equilibrium enthalpy of hydride decomposition, \( \Delta H_{d,eq} \), (\( \Delta H_{f,eq} = -\Delta H_{d,eq} \)) is, in magnitude, less than \( \Delta H_d \) and larger than \( \Delta H_f \). The relationship among them can be estimated from the equation

\[
\Delta H_f - \Delta H_d + 2|\Delta H_{eq}| = \frac{R}{2} \left( \frac{\partial \ln P_f}{\partial (1/T)} \right)_{H/W} + \frac{R}{2} \left( \frac{\partial \ln P_d}{\partial (1/T)} \right)_{H/W} - R \left( \frac{\partial \ln P_{eq}}{\partial (1/T)} \right)_{H/W}
\]

or,

\[
|\Delta H_{eq}| = -\frac{1}{2} \left( \Delta H_f - \Delta H_d \right) + \frac{R}{2} \left( \frac{\partial \ln (P_f/P_{eq})}{\partial (1/T)} \right)_{H/W}
\]

(4.1)

(4.2)

where \( P_f \) is the hydride formation pressure, \( P_d \) the hydride decomposition pressure and \( P_{eq} \) the equilibrium pressure. If the free energy loss due to hysteresis should be equal for hydride formation and decomposition it follows

\[
\Delta G_f = \frac{1}{2}RT \ln (P_f/P_{eq}) = \Delta G_d = \frac{1}{2}RT \ln (P_{eq}/P_d)
\]
or,

$$\ln \frac{P_r}{P_{eq}} = \ln \frac{P_{eq}}{P_d}$$

Then we have

$$\ln \frac{P_r P_d}{P_{eq}^2} = 0$$

and

$$|\Delta H_{eq}| = -\frac{1}{2} (\Delta H_r - \Delta H_d) \quad (4.3)$$

Equation 4.3 is proposed by Flanagan et al in Ref. 26 and is given here to show its general derivation and limitations. Average values of enthalpy and entropy (H/M = 0.2 - 0.7) for hydride formation and decomposition, and the absolute values of $\Delta H_{eq}$ calculated from equation 4.3 are listed in Table 4.3.

4.2 Hysteresis

All four Zr(FeCr)$_{2x}$ samples exhibit a remarkable hysteresis at the tested temperatures. The degree of hysteresis is generally best expressed by the logarithmic function, $1/2RT \ln P_r/P_d$, which is considered to be the free energy loss per mole of atomic hydrogen in completing a hysteresis loop [27-29]. Here this logarithmic function is
defined as the hysteresis factor.

4.2.1 Effects of Temperature and Alloy Composition

The hysteresis factor varies with temperature and alloy composition. Table 4.4 summarizes the effect of temperature on hysteresis in the Zr(Fe<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub> - H systems. All the samples behave the same as most metal-hydrogen systems, in that the hysteresis factor decreases with increasing temperature. The influence of temperature decreases with increasing x value. The hysteresis factor changes from 523 J mol<sup>-1</sup>H at 303.2K to 217 J mol<sup>-1</sup>H at 343.2K for x=0.5, about a 60% reduction while for x=0.8 the change is much smaller for the same temperature interval, the hysteresis factors being 1169 J mol<sup>-1</sup>H at 283.2K and 923 J mol<sup>-1</sup>H at 323.2K, only about a 20% difference.

The effect of alloy composition on hysteresis is shown by plotting 1/2RTlnP<sub>f</sub>/P<sub>d</sub> vs. x, Fig.4.5, where the hydrogen pressures are determined at H/M = 0.5 and T = 303.2K. With the increasing Fe substitution for Cr, the extent of hysteresis becomes larger. The hysteresis factor for x = 0.8 is twice that for x = 0.5 at 303.2K and almost three times at 323.2K (see Table 4.4). All Zr(Fe<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub> (x = 0 - 0.8) alloys have the same crystal structure, i.e., hexagonal MgZn<sub>2</sub> - type Laves phase, with lattice parameters decreasing with increasing x (Fe substitution) [26]. It seems, therefore, that hysteresis increases with decreasing lattice
parameters.

It has been observed for many hydride forming materials that the larger the interstitial hole size in the metal lattice which the hydrogen occupies, the more negative the free energy of hydride formation and the lower plateau pressure [107]. Therefore, for a given crystal structure there is a direct relationship between lattice parameters and plateau pressure. The decreasing lattice parameters will result in higher plateau pressures, as observed in the present samples. Based on this correlation of the plateau pressure as a function of interstitial hole size Lundin and Lynch [42] proposed that the difference between the plateau pressures for hydride formation and decomposition, and hence the magnitude of hysteresis, is due to the difference in the interstitial hole sizes associated with hydrogen absorption and desorption. The interstitial sites in either the α and β phases that are compressively strained in the absorption isotherm are relatively smaller than the sites in either the unstrained α and β phases in the desorption isotherm. This results in the higher pressures observed in the absorption isotherms compared to the desorption isotherms. No relationship, however, has been established between the magnitude of hysteresis and the interstitial hole size itself. It is interesting to speculate as to whether there is any direct link between increasing hysteresis and decreasing lattice parameters or the decrease of the interstitial hole
4.2.2 Effect of Hydrogen Aliquot Size

The effect of hydrogen aliquot size has also been found in the present samples. When small aliquots of hydrogen are added or removed in the two-phase coexistence region, the plateau pressure for hydride formation and decomposition are higher and lower, respectively, than when large aliquots are employed. The plateau pressures for hydride formation in Zr(Fe_{0.8}Cr_{0.2})_2 and Zr(Fe_{0.7}Cr_{0.3})_2 determined using large aliquot size and small aliquot size are shown in Fig. 4.6 and compared with those of LaNi_5. The change of hydrogen to metal ratio, Δ(H/M) is about 0.1 for large aliquot size and less than 0.005 for small aliquot size. The effect of aliquot size is expressed by 1/2RTlnP^S_f/P^L_f and listed in Table 4.5: P^S_f is the plateau pressure for hydride formation obtained from small aliquot size and P^L_f is that from large aliquot size. The effect of aliquot size for Zr(Fe_{x}Cr_{1-x})_2 is much smaller than that for LaNi_5, with the difference for Zr(Fe_{0.6}Cr_{0.4})_2 being too small to be shown on Fig. 4.6.

For a given sample size and measuring system, the hydrogen aliquot size affects the rate of hydride formation and decomposition or the interface velocity of phase transformation. Park and Flanagan [114, 117] proposed that the effect of aliquot size is actually the effect of the interface velocity. The large aliquot size leads to a rapid
interface velocity which destroys local interfacial equilibrium, resulting in a higher plateau pressure for hydride formation and a lower plateau pressure for hydride decomposition. The reaction kinetics of $\text{Zr(Fe}_x\text{Cr}_{1-x})_2$ are more rapid than that of $\text{LaNi}_5$. For the same aliquot and sample sizes and using the same experimental apparatus the hydrogen absorption and desorption rates of $\text{Zr(Fe}_x\text{Cr}_{1-x})_2$ are much faster than those of $\text{LaNi}_5$. Hydrogen absorption rate plots are shown in Fig. 4.7 for $\text{Zr(Fe}_{0.7}\text{Cr}_{0.3})_2$ and $\text{LaNi}_5$. In both instances, the hydrogen aliquots correspond to $\Delta(\text{H/M}) = 0.12$ and sample sizes are 4 grams. 90% of the total aliquot is absorbed by $\text{Zr(Fe}_{0.7}\text{Cr}_{0.3})_2$ within 75 seconds compared to about 250 seconds for $\text{LaNi}_5$. It seems difficult to explain with Park and Flanagan's model why the effect of aliquot size is much smaller while the interface velocity is much faster for $\text{Zr(Fe}_x\text{Cr}_{1-x})_2$ than for $\text{LaNi}_5$.

4.2.3 Effect of Hydrogen Absorption/Desorption Cycling

PC isotherms at 303.2K for the first three cycles of hydrogen absorption and desorption have been determined for $\text{Zr(Fe}_{0.5}\text{Cr}_{0.5})_2$, $\text{Zr(Fe}_{0.6}\text{Cr}_{0.4})_2$, $\text{Zr(Fe}_{0.7}\text{Cr}_{0.3})_2$ as well as $\text{LaNi}_5$, Figs. 4.8-4.11. It can be seen that the plateau pressures for hydride formation decrease and those for hydride decomposition increase and hence the magnitude of hysteresis is reduced with cycling. For $\text{LaNi}_5$, the hydride formation pressure during the first cycle is much higher than those.
during further cycles, whereas the hydride decomposition pressure does not change very much. For the Zr(Fe$_x$Cr$_{1-x}$)$_2$ alloys, the differences in hydride formation pressures between the first cycle and the further cycles are about the same as those for the hydride decomposition pressures. There are no experimentally detectable differences in the hydride decomposition pressures between the second and the third cycles for all three Zr(Fe$_x$Cr$_{1-x}$)$_2$ alloys. The differences in hydride formation pressures for the second and the third cycles for Zr(Fe$_x$Cr$_{1-x}$)$_2$ are also quite small. The effect of cycling on hysteresis, as expressed by a plot of $1/2RT\ln P_r/P_d$ vs. No. of cycles, is illustrated in Fig. 4.12. It is clear that the effect of cycling is more pronounced for LaNi$_5$ with the hysteresis factor for the first cycle being more than five times larger than that of the third cycle whereas for the Zr(Fe$_x$Cr$_{1-x}$)$_2$ alloys the ratio of the hysteresis factors for the first and the third is about two.

Wicke and coworkers [43, 129] have attributed the decrease of the plateau pressure of absorption during the first few cycles to the increasing fragmentation of the metal. They believe that the desorption branches of PC isotherm represent the true strain-free equilibrium and the absorption branches represent an equilibrium under mechanical constraints. The mechanical constraints are reduced due to the fragmentation of the metal, resulting in a lower plateau pressure of absorption. This strain model cannot explain why
the plateau pressures of desorption branches also change with cycling.

In their hysteresis model Lundin and Lynch [42] proposed that regardless of whether the particle size is large or small, the hysteresis effects are manifested at the atomic level, and hence the particle size (or the amount of cycling) has little effect on the presence of hysteresis. This is apparently not true for the first few cycles.

It seems to us that while the change of the mechanical constraints may be an important factor in the variation of plateau pressures with cycling a more important factor may be the changes of surface condition of the metal.

Hydrogen enters the lattice of intermetallic compounds in the atomic rather than molecular form. Therefore it has to be assumed that hydrogen becomes chemisorbed at the surface and dissociates into atoms as it enters the solid. The heat of dissociation is 425 KJ mol\(^{-1}\) H\(_2\). As the heat of hydride formation of all known metal-hydrogen systems is considerably lower, a special surface catalytic activity has to be postulated in all cases.

The structure of the near-surface region of well-defined samples has been determined by many researchers using various techniques such as AES, XPS, TEM, UV photoelectron spectroscopy (UPS), secondary ion mass spectroscopy (SIMS) and magnetic and resistivity measurements [157-164]. Surface segregation occurs in most intermetallic compounds. It has
been suggested that this surface segregation plays a prominent role in the activation process [144, 157-159]. Hydride forming intermetallic compounds normally consist of an element with a strong affinity for hydrogen (A) and one which absorbs little or no hydrogen at all (B) [165]. The element with the lowest surface energy (usually the A element) diffuses to the surface and bonds with any oxygen present in the hydrogen gas, forming an oxide and/or hydroxide. The B atoms are then present just below the surface as B or B-rich clusters. These clusters provide necessary active sites for hydrogen dissociation since the B element is frequently a middle-to-late transition metal and it is well known that hydrogen dissociates on these metals with little or no energy barrier [158, 159]. Molecular hydrogen can reach these clusters through gaps in the oxide (hydroxide) layer.

There is some question as to whether surface segregation is necessary for the alloy activation. A number of researchers have reported that surface segregation is not required for FeTi activation [161, 162, 167, 168]. It has been reported that no significant surface segregation is observed for ErFe₂ [169], ZrV₂ and ZrCr₂ [170]. The cracking and disintegration due to internal stresses, which result from large volume change accompanying phase transformation, generate a large fresh, clean surface. Metals with clean surfaces react very fast with hydrogen [171]. Any clean
surface may suffice to catalyze hydrogen dissociation.

No matter which mechanism is valid the same general conclusion can be reached, namely, that it is the changes in surface conditions of the sample that are responsible for the activation process. In the published literature the investigation into the activation process seems limited to the reaction kinetics rather than the "equilibrium" conditions as considered in this study. It seems to us that the surface condition would affect the time-invariant plateau pressures and the experimental evidence is shown in section 4.6 that the surface contamination do affect the plateau pressures. It is suggested here that the variation of plateau pressures and hysteresis with cycling during the first few cycles is largely due to the changes in the surface condition of the sample which affects the hydrogen dissociation and hydride (metal) nucleation process. Further discussion of these points can be found in Chapter 5.

4.3 Sloping Plateaus

Pronounced sloping plateau behaviors are found for Zr(Fe, Cr) hydrides (see Figs. 4.1 to 4.4). The sloping factors, defined by the plateau slope d(lnP)/(H/M), for these hydrides at various temperature are listed in Table 4.6. Plateau slopes increase with temperature for hydride decomposition but this same tendency is not observed for hydride formation.
From Table 4.6 we can also see the variation of sloping factors with the composition of host metals at constant temperatures. It seems there is no composition dependence of the sloping factors for hydride formation while the sloping factors for hydride decomposition generally increase with the increasing x (Fe substitution), e.g. the sloping factors at 303.2K for hydride formation are 0.90, 0.89, 0.92 and 0.90, and for hydride decomposition 0.50, 0.73, 1.03 and 1.03 with x value of 0.5, 0.6, 0.7 and 0.8, respectively.

The influence of temperature on the plateau slope for hydride decomposition decreases with increasing Fe content in host metals. The sloping factor increases by 54% over the temperature range from 303.2K to 343.2K for Zr(Fe0.5Cr0.5)2 hydride, 23% for Zr(Fe0.6Cr0.4)2 over the same temperature range, and 13% and 7% over the temperature range from 283.2K to 323.2K for Zr(Fe0.7Cr0.3)2 and Zr(Fe0.8Cr0.2)2 hydrides, respectively.

The effect of cycling during the first three cycles on the plateau slopes of Zr(FeCr1-x)2 hydrides is listed in Table 4.7. The plateau slopes decrease with cycling. The same phenomenon is also observed for LaNi5 hydride (see Fig. 4.11).

4.4 Lattice Strains Induced by Hydride Formation and Decomposition

X-ray diffraction line broadening of Zr(Fe0.75Cr0.25)2
was measured for annealed bulk and mechanically crushed powder samples and for those which had been subjected to one and five complete hydriding and dehydriding cycle(s). The integral line breadths of the annealed bulk sample are taken as the standard. The integral line breadths of the mechanically crushed powder are virtually the same as those of the annealed bulk sample. It has been reported [172] that an anneal of ground unactivated powder at 600°C in ultrahigh vacuum for three weeks produced no appreciable change in the shape of the diffraction lines for LaNi{5-x}Al{x} sample with a low degree of aluminum substitution. It can be concluded for these two intermetallic compounds, that the microstrains produced by the mechanically crushing process are negligible. The same may be true for other intermetallic compounds which are very brittle.

Significant line broadening is observed after the sample has been subjected to the hydride formation and decomposition cycle(s). The integral line breadths are plotted in Fig. 4.13 as \( (\beta^*)^2 \) against \( (d^*)^2 \) (Wagner and Aqua method) and in Fig. 4.14 as \( (\beta^*) \) against \( (d^*)^2/(\beta^*) \) (Halder and Wagner method). The line broadening is anisotropic and increases with cycling. The crystallite size and microstrains for reflection (110) (220) and (200) (300) are calculated from the intercepts and slopes respectively. The average values for all reflections except (004) are computed using the least-squares method. These results are listed in Tables 4.8
and 4.9.

The crystallite and microstrains obtained from both the Wagner and Aqua method and the Halder and Wagner method are in good agreement. The crystallite size is in the order of 0.1 μm. The reflection (hh0) contain larger microstrains than the reflection (h00). The average microstrains for all reflections except (004) are in the order of $1 \times 10^{-3}$.

The microstrains in the direction of the C axis could not be obtained directly due to the lack of two or more orders of the reflection (001) but they seems much smaller than those in the direction perpendicular to the C axis. If we assume that the crystallite size in reflection (004) is about the same as in all other reflections then there would be no microstrain in the C - direction.

The microstrains increase by 50% for the sample which had gone through five cycles compared to that which had gone through only one cycle. From PC isotherm measurements (see Figs. 4.8-4.10) we know that the effect of cycling on plateau pressures is limited to the first two or three cycles. It is highly likely that the effect of cycling on microstrains would also be limited to the first few cycles and hence it is reasonable to assume that the value of microstrains for five cycles would approximately be a saturated one, i.e. further cycling would produce essentially no more microstrains.

Line broadening has been reported [48, 58, 172, 173] in the neutron and X-ray diffraction patterns of LaNi$_5$ and
related intermetallic compounds, which have been subjected to the complete hydride formation and decomposition cycle(s), and of their hydrides. Dehydrided \( \text{LaNi}_5 \) contains strong and highly anisotropic microstrains. These microstrains may be remarkably reduced and may become isotropic for substituted \( \text{LaNi}_{5-x}M_x \) \( (M = \text{Mn, Al, Fe}) \) compounds [48, 172]. It is clear that the hydride formation and decomposition would induce microstrains and the magnitude of these microstrains is affected by the alloy composition.

In order to compare the particle size and the crystallite size, the particle sizes are determined for the same powder samples which are analyzed by X-ray diffraction. Representative micrographs are shown in Fig. 4.15 and size distribution plots are shown in Fig. 4.16. The mean particle size for the mechanically crushed powder is 292 \( \mu \text{m} \) with its standard deviation of 174 \( \mu \text{m} \) and those for dehydrided powders which have been subjected to one and five cycles are 22.2 \( \mu \text{m} \) and 15.5 \( \mu \text{m} \) respectively with their standard deviation of 8.3 \( \mu \text{m} \) and 8.2 \( \mu \text{m} \). The particle sizes of dehydrided powders are two orders larger than corresponding crystallite sizes (see Table 4.8 and 4.9) and hence a conclusion can be drawn that these dehydrided powders are polycrystalline materials.

4.5 Effect of Surface Contamination on Plateau Pressures

PC isotherms for hydrogen absorption of \( \text{LaNi}_5 \), with or without exposure to air before the measurements, are shown in
Fig. 4.17. The lowest curve was measured with a well activated sample (after 5 complete hydriding and dehydriding cycles). The sample was then fully dehydrided and exposed to air for 2 hours. The subsequent absorption PC isotherm was determined (middle curve). The sample was again fully dehydrided and cycled through 5 more phase conversions. It was fully recovered with virtually the same absorption PC isotherm as that before exposure to air, indicating that only the surface of the sample is affected when it is exposed to air. The highest curve was determined after exposing the dehydrided sample to air for 24 hours. It can be seen that the plateau pressure for hydride formation increased after the sample was exposed to air. The longer the sample was exposed to air, i.e., the more severe the surface contamination, the higher the plateau pressure. The plateau slope is also affected by the exposure of the sample to air, increasing from 0.08 for well activated sample to 0.17 for the sample which was exposed to air for 24 hours. An oxide layer(s) may form at the sample surface after the sample is exposed to air. This oxide product may block the active sites for hydrogen dissociation and hydride nucleation, resulting in higher plateau pressures.

4.7 Summary

(1) Substitution of iron for chromium in \( \text{Zr(Fe}_{x}\text{Cr}_{1-x})_2 \) remarkably raises the two-phase plateau pressures. The
average enthalpies (H/M = 0.2 - 0.7) for hydride formation are -17.2, -16.2, -12.9, -11.1 KJ/mol H and for hydride decomposition 19.5, 17.9, 15.0, 14.1 KJ/mol H with x = 0.5, 0.6, 0.7 0.8, respectively.

(2) Zr(Fe<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub> hydrides exhibit pronounced hysteresis over the temperature range from 283.2 to 353.2K.

(2.1) The degree of hysteresis decreases with increasing temperature and increases with increasing iron substitution for chromium whereas the influence of temperature on hysteresis decreases with increasing iron content in host alloys. The hysteresis factors, 1/2RTlnP<sub>f</sub>/P<sub>d</sub>, range from 217 J/mol H for x = 0.5 at T = 343.2K to 1169 J/mol H for x = 0.8 at 283.2K.

(2.2) The magnitude of hysteresis determined with large aliquots is smaller than that determined with small aliquots. This effect of aliquot size is quite small compared with that of LaNi<sub>5</sub> hydride.

(2.3) Hysteresis is reduced during the first few cycles of hydride formation and decomposition. Again this effect of cycling is quite small compared with that of LaNi<sub>5</sub> hydride. It is suggested that the variation of plateau pressures and hysteresis with cycling during the first few cycles is largely due to the changes in the surface condition of the sample.

(3) Significant sloping plateau behaviors are observed for Zr(Fe<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub> hydrides. There is no apparent dependence
of the plateau slopes on temperature and alloy composition for hydride formation while the plateau slopes for hydride decomposition seem increasing with increasing temperature and Fe content. The influence of temperature on plateau slopes for hydride decomposition decreases with the increasing Fe substitution for Cr. The plateau slopes for hydride formation are about 0.9 and those for hydride decomposition range from 0.5 to 1.1. Similar to hysteresis the plateau slopes decrease with cycling during the first few cycles of hydride formation and decomposition.

(4) Strong broadening of X-ray diffraction lines is observed for Zr(Fe$_{0.75}$Cr$_{0.25}$)$_2$ which has been subjected to the complete cycle(s) of hydride formation and decomposition. The line broadening is anisotropic and increases with cycling. The microstrains in the direction perpendicular to the c axis are much larger than those parallel to the c axis. The average crystallite size for all reflections except (001) is in the order of 0.1 μm and the corresponding average microstrains are in the order of 1 x 10$^{-3}$.

(5) The surface condition will affect the plateau pressures. The subsequent plateau pressure for hydride formation and its slope increase after a fully dehydrided sample is exposed to air. The longer the sample is exposed to air, i.e. the more severe the surface contamination, the higher the plateau pressure and the larger the plateau slope.
Table 4.1 Enthalpy and entropy for hydride formation of Zr(Fe<sub>x</sub>Cr<sub>1-x</sub>) - H systems as derived from PC isotherms by means of the van't Hoff plots

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Table 4.2 Enthalpy and entropy for hydride decomposition of Zr(Fe$_{\frac{x}{2}}$Cr$_{1-x}$)$_2$-H systems as derived from PC isotherms by means of the van't Hoff plots

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<tr>
<td></td>
<td>0.3</td>
<td>14.2±0.5</td>
<td>52.0±0.9</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>14.3±0.4</td>
<td>52.8±0.8</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>14.2±0.2</td>
<td>52.9±0.3</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>13.9±0.2</td>
<td>52.3±0.3</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>13.8±0.2</td>
<td>52.5±0.3</td>
</tr>
</tbody>
</table>
Table 4.3  Average enthalpy and entropy (H/M = 0.2-0.7) for hydride formation and decomposition of Zr(Fe,Cr)\textsubscript{1-x}\textsubscript{2} from van't Hoff plots and the equilibrium enthalpy calculated from equation 4.3

| x  | Δ\textsubscript{H}\textsubscript{r}  | Δ\textsubscript{H}\textsubscript{d} | |Δ\textsubscript{H}\textsubscript{eq}| | Δ\textsubscript{S}\textsubscript{r} | Δ\textsubscript{S}\textsubscript{d} |
|----|------------------|------------------|------------------|------------------|------------------|------------------|
|    | (KJ /mol H)      | (KJ /mol H)      | (JK /mol H)      | (JK /mol H)      | (JK /mol H)      | (JK /mol H)      |
| 0.5| -17.2±0.4        | 19.5±0.7         | 18.4±0.6         | -48.9±1.6        | 54.7±2.6         |
| 0.6| -16.2±0.3        | 17.9±0.4         | 17.1±0.4         | -50.7±1.3        | 54.5±1.8         |
| 0.7| -12.9±0.1        | 15.5±0.9         | 14.0±0.5         | -48.5±0.7        | 52.6±1.6         |
| 0.8| -11.1±0.2        | 14.1±0.2         | 12.6±0.2         | -46.0±0.9        | 52.3±0.6         |
Table 4.4 Effect of temperature on hysteresis in Zr(Fe\textsubscript{x}Cr\textsubscript{1-x})\textsubscript{2} - H systems

<table>
<thead>
<tr>
<th>( x )</th>
<th>Temp. (K)</th>
<th>( P^*_f ) (Kpa)</th>
<th>( P^*_d ) (Kpa)</th>
<th>( 1/2RT\ln P^<em>_f / P^</em>_d ) (J/mol H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>303.2</td>
<td>15.6</td>
<td>10.3</td>
<td>523</td>
</tr>
<tr>
<td></td>
<td>323.2</td>
<td>36.3</td>
<td>28.0</td>
<td>349</td>
</tr>
<tr>
<td></td>
<td>343.2</td>
<td>76</td>
<td>64</td>
<td>217</td>
</tr>
<tr>
<td>0.6</td>
<td>303.2</td>
<td>55</td>
<td>34</td>
<td>606</td>
</tr>
<tr>
<td></td>
<td>323.2</td>
<td>120</td>
<td>85</td>
<td>463</td>
</tr>
<tr>
<td></td>
<td>343.2</td>
<td>235</td>
<td>180</td>
<td>380</td>
</tr>
<tr>
<td>0.7</td>
<td>283.2</td>
<td>220</td>
<td>96</td>
<td>1045</td>
</tr>
<tr>
<td></td>
<td>303.2</td>
<td>450</td>
<td>220</td>
<td>902</td>
</tr>
<tr>
<td></td>
<td>323.2</td>
<td>860</td>
<td>460</td>
<td>789</td>
</tr>
<tr>
<td>0.8</td>
<td>283.2</td>
<td>540</td>
<td>200</td>
<td>1169</td>
</tr>
<tr>
<td></td>
<td>303.2</td>
<td>1010</td>
<td>435</td>
<td>1061</td>
</tr>
<tr>
<td></td>
<td>323.2</td>
<td>1770</td>
<td>890</td>
<td>923</td>
</tr>
</tbody>
</table>

* at H/M = 0.5
Table 4.5 Effect of aliquot size on hysteresis in Zr(Fe,Cr\textsubscript{1-x})\textsubscript{2} - H and LaNi\textsubscript{5} - H systems

<table>
<thead>
<tr>
<th></th>
<th>LaNi\textsubscript{5}</th>
<th>Zr(Fe,Cr\textsubscript{1-x})\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x=0.6</td>
<td>x=0.7</td>
</tr>
<tr>
<td>(P_f)\textsuperscript{s} (Kpa)</td>
<td>312</td>
<td>.54</td>
</tr>
<tr>
<td>(P_f)\textsuperscript{l} (Kpa)</td>
<td>276</td>
<td>52</td>
</tr>
<tr>
<td>(1/2RT\ln P_f)\textsuperscript{s}/(P_f)\textsuperscript{l} (J/mol H)</td>
<td>154</td>
<td>48</td>
</tr>
</tbody>
</table>

* \(T = 303.2\text{K}, \text{H/M} = 0.4\)
Table 4.6 The effect of temperature and alloy composition on the plateau slope for Zr(Fe\textsubscript{x}Cr\textsubscript{1-x}\textsubscript{2}) hydrides

<table>
<thead>
<tr>
<th>x</th>
<th>T(K)</th>
<th>dlnP\textsubscript{f}/d(H/M)</th>
<th>dlnP\textsubscript{d}/d(H/M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>303.2</td>
<td>0.90</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>323.2</td>
<td>0.90</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>343.2</td>
<td>0.87</td>
<td>0.77</td>
</tr>
<tr>
<td>0.6</td>
<td>303.2</td>
<td>0.89</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>323.2</td>
<td>0.97</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>343.2</td>
<td>0.92</td>
<td>0.90</td>
</tr>
<tr>
<td>0.7</td>
<td>283.2</td>
<td>0.91</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>303.2</td>
<td>0.92</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>323.2</td>
<td>0.88</td>
<td>1.08</td>
</tr>
<tr>
<td>0.8</td>
<td>283.2</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>303.2</td>
<td>0.90</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>323.2</td>
<td>0.81</td>
<td>1.05</td>
</tr>
</tbody>
</table>
Table 4.7 The effect of cycling on the plateau slope for Zr(Fe$_x$Cr$_{1-x}$)$_2$ hydrides (T = 303.2K)

<table>
<thead>
<tr>
<th>$x$</th>
<th>No. of cycles</th>
<th>$\frac{d\ln P_f}{d(H/M)}$</th>
<th>$\frac{d\ln P_d}{d(H/M)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1</td>
<td>0.92</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.90</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.90</td>
<td>0.50</td>
</tr>
<tr>
<td>0.6</td>
<td>1</td>
<td>1.20</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.89</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.89</td>
<td>0.73</td>
</tr>
<tr>
<td>0.7</td>
<td>1</td>
<td>1.26</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.94</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.92</td>
<td>1.03</td>
</tr>
</tbody>
</table>
Table 4.8 Crystallite size and microstrains
determined with Wagner and Aqua method [155]

<table>
<thead>
<tr>
<th>Reflection</th>
<th>No. of cycles</th>
<th>D \times 10^{-3}(\text{A})</th>
<th>\varepsilon \times 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110) (220)</td>
<td>1</td>
<td>1.23</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.96</td>
<td>1.79</td>
</tr>
<tr>
<td>(200) (300)</td>
<td>1</td>
<td>1.45</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.09</td>
<td>1.74</td>
</tr>
<tr>
<td>Average *</td>
<td>1</td>
<td>1.28</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.15</td>
<td>1.81</td>
</tr>
</tbody>
</table>

* All reflections except (004)
Table 4.9 Crystallite size and microstrains
determined with Halder and Wagner method [156]

<table>
<thead>
<tr>
<th>Reflection</th>
<th>No. of cycles</th>
<th>$D \times 10^{-3} \text{(A)}$</th>
<th>$\varepsilon \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110) (220)</td>
<td>1</td>
<td>1.51</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.25</td>
<td>1.64</td>
</tr>
<tr>
<td>(200) (300)</td>
<td>1</td>
<td>1.66</td>
<td>1.07</td>
</tr>
<tr>
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<td>5</td>
<td>1.39</td>
<td>1.56</td>
</tr>
<tr>
<td>Average</td>
<td>1</td>
<td>1.39</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.21</td>
<td>1.63</td>
</tr>
</tbody>
</table>

* All reflections except (004)
Fig. 4.1 PC isotherms for $\text{Zr(Fe}_{0.5}\text{Cr}_{0.5})$--H system. $O$, 303.2K; $\Delta$, 323.2K; $\Box$, 343.2K. Filled symbols correspond to absorption data and open symbols to desorption data.
Fig. 4.2 PC isotherms for Zr(Fe_{0.6}Cr_{0.4})_2-H system. The symbols have the same meaning as in Fig. 4.1.
Fig. 4.3 PC isotherms for Zr(Fe<sub>0.7</sub>Cr<sub>0.3</sub>)<sub>2</sub>–H system. • 0, 283.2K; ▲ Δ, 303.2K; ■ ○, 323.2K. Filled symbols correspond to absorption data and open symbols to desorption data.
Fig. 4.4 PC isotherms for Zr(Fe_{0.8}Cr_{0.2})_2-H system. The symbols have the same meaning as in Fig. 4.3.
Fig. 4.5 Effect of alloy composition on hysteresis in 
Zr(Fe$_x$Cr$_{1-x}$)$_2$-H system (T = 303.2K and H/M = 0.5).
Fig. 4.6 Values of the absorption plateau pressures at 323.2K and H/M = 0.4. --, large aliquot size; ----, small aliquot size. Δ(H/M) is about 0.1 for large aliquot size and less than 0.005 for small aliquot size.
Fig. 4.7 Hydrogen absorption rates for Zr(Fe$_{0.7}$Cr$_{0.3}$)$_2$ and LaNi$_5$ determined with the same aliquot size and sample size (6th absorption and desorption cycle, 303.2K). Upper curve, Zr(Fe$_{0.7}$Cr$_{0.3}$)$_2$; lower curve, LaNi$_5$. 
Fig. 4.8 PC isotherms for Zr(Fe_{0.5}Cr_{0.5})-H system at 303.2K.
- O, 1st cycle; ▲ Δ, 2nd cycle; ■ □, 3rd cycle. Filled symbols correspond to absorption data and open symbols to desorption data.
Fig. 4.9 PC isotherms for Zr(Fe₀.₆ Cr₀.₄)₂-H system at 303.2K.

The symbols have the same meaning as in Fig. 4.8.
Fig. 4.10 PC isotherms for Zr(Fe_{0.7}Cr_{0.3})_2-H system at 303.2K. The symbols have the same meaning as in Fig. 4.8.
Fig. 4.11 PC isotherms for LaNi$_5$-H system at 303.2K. The symbols have the same meaning as in Fig. 4.8.
Fig. 4.12 \((1/2RT\ln P/P_a)\) vs. the number of cycles at \(H/M = 0.5\) and \(T = 303.2K\). 
- \(\bullet\), \(\text{LaNi}_5\); 
- \(\triangledown\), \(\text{Zr(Fe}_{0.7}\text{Cr}_{0.3})_2\); 
- \(\blacksquare\), \(\text{Zr(Fe}_{0.6}\text{Cr}_{0.4})_2\); 
- \(\blacktriangle\), \(\text{Zr(Fe}_{0.5}\text{Cr}_{0.5})_2\).
Fig. 4.13 Plots of Wagner and Aqua method [155] for X-ray diffraction line broadening of Zr(Fe$_{0.75}$Cr$_{0.25}$)$_2$ due to hydride formation and decomposition cycles. ▲, after one cycle; ●, after five cycles.
Fig. 4.14 Plots of Halder and Wagner method [156] for X-ray diffraction line broadening of Zr(Fe<sub>0.75</sub>Cr<sub>0.25</sub>)<sub>2</sub> due to hydride formation and decomposition cycles. ▲, after one cycle; ●, after five cycles.
Fig. 4.15 SEM micrographs for \( \text{Zr(Fe}_{0.75}\text{Cr}_{0.25})_2 \) showing particle size distribution. Upper graph, after one cycle; lower graph, after five cycles.
Fig. 4.16 Histogram distribution of particle size for $\text{Zr(Fe}_{0.75}\text{Cr}_{0.25})_2$.
Fig. 4:17 PC isotherms of hydrogen absorption for LaNi$_5$ at 30°C. △, activated sample; △, after exposure to air for 2 hours; ◊, after exposure to air for 24 hours.
CHAPTER 5
PROPOSED MODEL

From the published experimental results and experimental observations in this investigation, it is clear that hysteresis in metal-hydrogen systems is very complex. Not only many experimental variables affect hysteresis, including temperature, composition, aliquot size, cycling, annealing, particle size and surface contamination, but also one particular variable may affect hysteresis in a different manner in different systems (see Table 2.4 and related sections in the previous chapter).

The existing theoretical models can be generally divided into two groups (see Table 2.5). In the first group, the origin of hysteresis is believed to be a strain effect in hydride formation. Because of the large volume expansion the hydride grows under a compressive stress. The desorption of only a small amount of hydrogen is all that is required to relax the residual elastic forces so that the phase is no longer under stress. Hence the desorption branches of the hysteresis loop of a PC isotherm represent the true strain free equilibrium whereas the absorption branches represent, instead, an equilibrium under mechanical constraints. In this group, one model [38] is based on the quantitative calculation of the elastic strain energy for hydrogenation.
and hysteresis is considered to be primarily a consequence of this elastic strain energy, whereas in other strain models the elastic accommodation and plastic accommodation are not well distinguished.

In the second group of models, it is argued that hysteresis results from the free energy dissipation due to plastic deformation which accompanies the phase conversion, and the same amount of plastic deformation occurs during hydride formation and decomposition. Therefore, it is proposed that the true equilibrium is located halfway between the absorption and the desorption branches. The effect of elastic accommodation is excluded by the argument that this effect is thermodynamically reversible and hence should not affect hysteresis [80, 84, 121] or by the assumption that the internal stresses resulting from phase conversion are completely relaxed by plastic deformation [29].

Both groups of models are supported by experimental results. Nevertheless, none of these seems to be adequate to explain the complete range of experimentally observed behavior. In this chapter a generalized model for hysteresis and sloping plateaus in metal-hydrogen systems is proposed. The effect of temperature, composition, aliquot size, cycling, annealing and particle size on plateau pressures and hysteresis are explained.
5.1 Hydride Formation and Decomposition Process

The formation of metal hydride by the reaction of gaseous hydrogen with metal, represented by Eq. 1.1, consists of a sequence of elementary steps [175-177]. Hydrogen has to pass various intermediate states before it reaches the reaction zone.

From structural studies and the shape of the PC isotherms in the $\alpha$ phase region, it is well known that hydrogen is dissolved as an atomic or non-molecular species in the metal lattice. The molecular hydrogen gas has to be dissociated at the metal surface in the absorption process and the hydrogen atoms recombine to hydrogen molecules in the desorption process. The heat of dissociation or recombination may result in a very high energy barrier.

The curves of potential energy as a function of the distance from the metal surface for an hydrogen molecule and for two hydrogen atoms have been calculated for the interaction of gaseous hydrogen with a clean, smooth metal surface (Fig. 5.1) [178]. Away from the surface, the two curves are separated by the heat of dissociation, $E_D$ ($= 425$ KJ/mol H$_2$). The flat minimum in the molecular hydrogen and metal curve corresponds to physisorbed H$_2$ with a heat of physisorption, $E_p$ (<30 KJ/mol H$_2$). The deep minimum in the atomic hydrogen and metal curve corresponds to chemisorbed H with a heat of chemisorption $E_{HC}$ ($= 100$ KJ/mol H$_2$). If the two curves intersect at a point above the zero energy level...
(which is equal to the potential energy of $H_2$ far away from
the surface), the chemisorption requires an activation energy
$E_{c_A}$. Intersection below the zero energy level allows for
non-activated chemisorption.

A hydrogen molecule impinging on the metal surface can be
physisorbed or dissociatively chemisorbed depending on its
kinetic energy and the height of the activation energy
barrier. Next, the chemisorbed hydrogen atoms penetrate the
surface and dissolve in the bulk. An additional activation
energy may be required for penetration. Exothermic solution
of chemisorbed hydrogen atoms requires an energy $E_{\text{HC}}-E_s$. Bulk
diffusion requires an activation energy, $E_{\text{diff}}$. If hydrogen
is dissolved endothermically, an energy equal to $E_{\text{HC}}+E_s$ is
needed. As long as this energy is not supplied, hydrogen
atoms remain chemisorbed at the surface.

Bulk diffusion proceeds until some limiting concentration
of the dissolved hydrogen is exceeded and the nucleation and
growth of the hydride phase takes place. The density of the
hydride formed is lower than that of the parent metal. The
development of a hydride phase in a metallic matrix is thus
accompanied by a strain field resulting from this volume
expansion. The magnitude of the strain energy depends on the
difference between the density of the hydride and that of the
parent metal, the mechanical properties of these materials,
and, for the powder materials, the particle size. The
formation of a hydride phase also creates an interface
between hydride and metal, associated with which is an
interface energy. These additional energy terms may affect
both the thermodynamic and the kinetic characteristics of the
hydrogenation reaction.

The elementary steps involved in hydrogen absorption
resulting in hydride formation can be summarized as

(1) Mass transport of hydrogen molecules to the metal
surface.

(2) Molecular adsorption (physisorption) of hydrogen on
the metal surface.

(3) Dissociative adsorption (chemisorption) of hydrogen
on the metal surface.

(4) Transition of chemisorbed hydrogen atoms into the
bulk.

(5) Solid state diffusion of hydrogen atoms in the bulk.

(6) Nucleation and growth of the hydride phase.

The last step is accompanied by a large volume expansion
and the resulting strain field. Due to the large reaction
heat and poor thermal conductivity of the hydrides, the heat
transfer effect will dominate the kinetics under the
experimental conditions that permit a very fast reaction rate
[179-182]. However, the effects associated with heat transfer
as well as mass transfer are negligible in the evaluation of
plateau pressures since what is concerned with here is
time-independent properties.

Hydride decomposition takes place essentially in a
reverse sequence. First, the metal phase nucleates and grows from the hydride phase, and hydrogen atoms diffuse through the metal or hydride phase to the surface to reach the chemisorbed condition. Then hydrogen atoms have to recombine to hydrogen molecules and finally they leave the surface (associative desorption). The activation energy for desorption is $E_{HC} + E^*_{C,A}$ or $E_{HC} - E^*_{C,NA}$ on an activated or a non-activated surface respectively. For hydrogen to desorb, hydrogen atoms must gain extra energy to overcome the heat of solution or heat of chemisorption.

Among the elementary steps discussed above, dissociative chemisorption or associative desorption, and nucleation and growth are fundamentally more important, especially when one deals with the time-independent phenomena of hysteresis and sloping plateaus. These two steps will be discussed in more detail in the following sections.

5.2 Hydrogen Dissociative Absorption and Associative Desorption

A large number of experimental and theoretical papers concerning the chemisorption of hydrogen on metals have been published (see, for example, Refs.[183-188]).

The activation energy for chemisorption $E^*_{C,A}$ and heat of chemisorption $E_{HC}$, and more generally the shape of the potential energy curves shown in Fig. 5.1 depend on the surface conditions (crystal orientation, roughness and
cleanliness). Surface roughness and defects such as lattice steps may affect hydrogen absorption and desorption [189,190]. The more significant effect on the surface properties is surface contamination as reflected in the variation of the sticking probability and the activation energy for chemisorption.

The sticking probability $S$ is the probability that a reactive gas molecule impinging on the surface will dissociate and that the resulting atoms will stick to the surface in chemisorption sites. For clean surfaces of many transition metals the sticking probability of molecule hydrogen at zero coverage is close to unity, $S \approx 1$ and the activation energy for chemisorption of hydrogen is close to zero, $E_c \approx 0$, i.e. hydrogen adsorption on clean transition metals is a non- or only weakly activated process [183, 187]. The strong reactivity of transition metals has been correlated with the presence of unpaired d electrons in these metals and their participation in the formation of a strong chemisorption bond [191, 192]. The metals copper, silver and gold, which have filled d-bands, are known to have an activation barrier for hydrogen chemisorption [192].

The presence of small amounts of impurities on the surface of metals, however, can set up an energy barrier for dissociative chemisorption of hydrogen and reduce the sticking probability substantially [192-198]. Based on self-consistent calculations of the electronic structure of
adsorbed electropositive and electronegative atoms Norskov et al. [192] come to the conclusion that an energy barrier for dissociation can be created by the presence of electronegative atoms on the surface, which screen the influence of the incompletely filled d-bands. The range of this screening effect can be estimated to about one nearest neighbor distance. This explains why less than one monolayer of electronegative atoms is sufficient to suppress the sticking probability [192, 196].

With the increasing amounts of impurities, surface layers (e.g. oxides, hydroxides, carbides) may form on the metal surfaces. These surface layers may impede or prevent hydrogen absorption and desorption. It is desirable to distinguish between protective and non-protective surface layers. A protective surface layer prevents the reaction of the underlying metal with adsorbed atoms. For metals covered by protective oxide overlayers, additional reaction steps in the near-surface region of the metal must be included. The reaction steps (2)-(4) discussed in the previous section should be modified as [171]

(2) Molecular adsorption (physisorption) of hydrogen on the oxide surface.

(3) Dissociative adsorption (chemisorption) of hydrogen on the oxide surface.

(4) Transition of chemisorbed hydrogen atoms into the oxide.
(5) Hydrogen diffusion in the oxide.

(6) Transition of hydrogen atoms from the oxide to the metal or hydride phase.

Any of the steps above may set up, or increase, the energy barrier thus retarding or inhibiting hydrogen absorption or desorption. Passivation can be caused by slow dissociation of hydrogen molecules on the surface, slow transfer of chemisorbed hydrogen atoms into the oxide, or slow permeation of hydrogen atoms through the oxide layer.

Many experimental results have been reported on the effects of surface layers on the hydrogen absorption and desorption. Oxide layers prevent the solution of hydrogen in, for example, niobium, tantalum and vanadium [194, 199-201]. Oxidation of the surface can be used to seal the surface of the hydride to avoid hydrogen desorption [202]. The hydride can be stored in air for long periods without loss of hydrogen after it is exposed to O₂, CO and S0₂. The surface-coating with a thin layer of palladium can avoid or reduce the deactivation on exposure to air [203]. In the case of Niobium and tantalum, the sticking probability reaches unity for palladium layers of the order of three monolayers thick [204,205].

The high activation energy between the physisorbed and the chemisorbed states of hydrogen on an oxidized surface prevents dissociative chemisorption and associative desorption. The sticking probability is nearly zero.
Molecular hydrogen cannot penetrate the protective surface layer to dissociate on the underlying metallic surface and dissolved atomic hydrogen cannot leave the surface because of the inhibition of the recombination of hydrogen atoms to hydrogen molecules. Coating of the surface with palladium prevents the formation of a stable protective oxide layer. Dissociative chemisorption and associative desorption can occur easily on palladium. Furthermore, the palladium layer lowers the activation energy barrier to the migration of the chemisorbed hydrogen into the bulk.

In the case of non-protective oxide layers, hydrogen can slowly penetrate the surface layer and reach the underlying metallic surface to be dissociated. The surface layer cracks due to the volume expansion accompanying the initial hydride formation. The reaction then speeds up. If the hydrogenation disintegrates the host metal, a clean surface is produced and the energy barrier for dissociative chemisorption is reduced or eliminated.

In summary, the energy barrier for the dissociative absorption or associative desorption of hydrogen in clean transition metals and probably many other metals (alloys and intermetallic compounds) which form metal hydrides is non-existent or very small whereas the surface contamination (adsorption of small amounts of impurities or the formation of surface layers such as oxides) may create a large energy barrier or greatly increase it. Due to this large energy
barrier the reaction rate can be negligibly small at low temperatures and the reaction may even be totally blocked if this energy is not supplied externally by the increase of hydrogen chemical potential.

5.3 Elastic and Plastic Accommodation of the Volume Change due to Hydride Formation and Decomposition

Hydrogen dissolved in metals occupies interstitial sites in the host lattice. In all known metal-hydrogen systems the dissolved hydrogen expands the crystal lattice of the host metal. Each hydrogen interstitial causes displacements of the metal atoms from their regular sites, resulting in crystal lattice distortions (described as strain or stress fields). A variety of phases may be formed with different hydrogen concentrations. The phase with high hydrogen concentration is less dense than that with low hydrogen concentration. Typical relative volume differences associated with $\Delta(H/M) = 1$ are of the order of 20%.

The volume change of phase transformation can be accommodated by: (1) diffusion of the metal atoms; (2) elastic distortion; (3) plastic deformation and (4) relaxation through free surface. At the low temperatures of interest, the matrix cannot accommodate this volume change by diffusion of the metal atoms. Hence phase transformations are accompanied by elastic distortion and the resulting internal stresses. When the internal stresses exceed the yield stress
of the metallic crystal, the crystal will undergo plastic deformation rather than remain in a purely elastic state. There are three typical cases (Fig. 5.2). (1) In the case of ideal plastic behavior, phase transformation takes place at a constant yield stress and the volume change is accommodated by elastic distortion and plastic deformation. (2) If there is significant strain-hardening, i.e. the stress for further plastic deformation increases with phase transformation, the fracture strength of the specimen may be exceeded and the crystal fractures. (3) For brittle materials (most intermetallic compounds) the fracture strength will be exceeded with little or no plastic deformation. In the latter two cases, in addition to elastic and plastic accommodation, the internal stresses are able to relax through a free surface after the specimen is disintegrated into a powder. Relaxation through a free surface is also possible when the new phase is formed at or near a free surface and when the size of the new phase approaches the size of the specimen.

Lee et al. [206] developed analytical expressions for the accommodation energy of an isotropic matrix containing a misfitting spherical precipitate for both the pure elastic case and the case when plastic deformation takes place (assuming ideal plastic behavior).

In a purely elastic state, the radial and tangential elastic stresses within the precipitate are
\[ \sigma_r^p = \sigma_\theta^p = -4\mu\beta E c = -P \]  

(5.1)

and those in the matrix are

\[ \sigma_r^M = -2\sigma_\theta^M = -4\mu\beta E c (a/r)^3 = -P(a/r)^3 \]  

(5.2)

The expression for \( \beta E \) is

\[ \beta E = \alpha\gamma/[(\gamma-1)+1] \]  

(5.3)

and

\[ \alpha = (1+\nu)/3(1-\nu) \]  

(5.4)

Where \( \mu \) and \( \nu \) are the shear modulus and Poisson’s ratio of the matrix phase, respectively, \( \varepsilon \) is the radial stress-free misfit strain of the precipitate, \( \gamma \) is the ratio of the bulk modulus of the precipitate to that of the matrix, \( a \) is the spherical precipitate radius, \( r \) is the radical distance from the center of the precipitate and \( P \) is the internal hydrostatic pressure in the precipitate.

The expression for the total strain energy associated with a misfitting spherical precipitate in a purely elastic state, per unit volume of the precipitate is

\[ E_{ei} = 6\mu\beta E \varepsilon^2 = \frac{3}{2} \ P \varepsilon \]  

(5.5)
The elastic distortion alone is unable to accommodate the large volume change due to hydride formation and decomposition. The matrix will yield as the internal stress increases. The yielding condition is obtained by adopting the von Mises yielding criterion [207], namely that yielding occurs when an equivalent stress $\sigma_e$ exceeds the yield stress $\sigma_y$, where $\sigma_e$ is given by

$$\sigma_e = \sigma_0 - \sigma_r \quad (5.6)$$

Substitution of (5.2) into (5.6) yields

$$\sigma_e = -\frac{3}{2} P \frac{(a/r)^3}{3} \quad (5.7)$$

Therefore yielding will start at the matrix - precipitate interface when the pressure $P$ reaches the critical value $2\sigma_y/3$. As the internal pressure $P$ increases beyond the critical value, a plastic zone develops adjacent to the matrix - precipitate interface, extending to a radius depending upon the magnitude of $P$, and the crystal is in a elasto-plastic state, Fig.5-2. The precipitate is considered to remain in a purely elastic state since the stress state within the spherical precipitate is hydrostatic (Eq.5.1) and a hydrostatic stress state does not induce yielding.

In the elasto-plastic state the internal hydrostatic pressure in the precipitate is given by
\[ P = 3K\gamma \epsilon (1-\beta^{E+P}) \quad (5.8) \]

and \( \beta^{E+P} \) is obtained from

\[ 6\alpha \mu c(\gamma + \beta^{E+P} - \gamma\beta^{E+P})/\sigma_y = \exp\{[9K\gamma \epsilon (1-\beta^{E+P})/2\sigma_y]-1\} \quad (5.9) \]

where \( K \) and \( \sigma_y \) are bulk modulus and the yield stress of the matrix, respectively.

The total accommodation energy involved in elasto-plastic deformation, \( W \), is the sum of the elastic energy inside the precipitate, \( W_{E,\text{ppt}} \), the elastic and plastic energies in the plastic zone, \( W_{E,\text{in}} \) and \( W_{E,\text{out}} \), and the elastic energy outside the plastic zone, \( W_{E,\text{out}} \).

The plastic strain energy is given by

\[ W_P = \sigma_y^2 \left( (r_p/a)^3 \ln(r_p/a) - (r_p/a)^3 + 1/3 \right) / \alpha \mu \quad (5.10) \]

The total elastic energy is

\[ W_E = W_{E,\text{ppt}} + W_{E,\text{in}} + W_{E,\text{out}} \]

\[ = \frac{P^2(1-\gamma)}{2\gamma K} + \sigma_y^2 \left( (r_p/a)^3 - 1/2 \right) / 3\alpha \mu \quad (5.11) \]

and then the total accommodation energy is

\[ W = W_P + W_E \]

\[ = \frac{P^2(1-\gamma)}{2\gamma K} + \sigma_y^2 \left( 1/6 + (r_p/a)^3 \ln(r_p/a) \right) / \alpha \mu \quad (5.12) \]
where all accommodation energies are per unit volume of the precipitate, \( r_p \) is the plastic zone radius which depends on the magnitude of \( P \)

\[
    r_p = a \exp \left( \frac{P}{2\sigma_y} - 1/3 \right) \tag{5.13}
\]

Equations (5.1) to (5.13) correspond to the case of \( c > 0 \). In the case of \( c < 0 \), the only change required is to replace \( \sigma_y \) with \( -\sigma_y \).

The accommodation energies in the elasto-plastic state depend on the yield stress. Lee et al. [206] proposed that the effective yield stress is dependent on the size of precipitates. When a precipitate is of the order of a micron or above, the effective yield stress is identified as a macroscopic yield stress while for submicro precipitates size-dependent yield stresses are deduced from the Ashby-Johnson model [208]. In the case of coherent submicron precipitates, the effective yield stress becomes the theoretical yield strength, and thus plastic relaxation is not possible unless the transformation stress is extremely large. For incoherent submicron precipitates, the effective yield stress is approximately inversely proportional to the precipitate radius, \( r \), and hence plastic relaxation again is not possible when \( r < 10 \) nm. It was shown [206] that when plastic relaxation is possible the stress and strain distributions are altered quite drastically for a soft
material in the elasto-plastic state relative to those in the purely elastic state. The strain energy can be reduced by a factor of 15 at a misfit of 3% through plastic relaxation, i.e. for $\varepsilon = 0.03$ and $\sigma_y = 10^{-3}\mu$ the total accommodation energy is only about 0.07 times the pure linear elastic accommodation energy

$$\frac{W}{E_{cl}} = 0.07 \quad (5.14)$$

Moreover, the plastic component of this reduced energy dominates

$$\frac{W_P}{W} = \frac{W_P}{W_P + W_E} = 0.78 \quad (5.15)$$

or $W_P \ll W_E$. Lowering $\sigma_y$ will further decrease the first ratio (Eq.5.14) and increase the second (Eq.5.15).

A subsequent paper [209] extended the above calculations to the case of linear and power law strain-hardening behavior. It is shown that, as the strain-hardening parameter increases (the slope of the plastic stress-strain curve approaching that of the elastic curve), the ratio in Eq.5.14 increases towards the limiting value of one, whereas that of Eq.5.15 decreases towards the limiting value of zero. That is to say, for a highly strain-hardening material, plastic accommodation will, in contrast to an ideal plastic material, reduce the total accommodation energy by only a small amount.
and most of this remaining energy will be in the form of elastic energy.

The strain-hardening of Pd-H system in the α + β phase transformation has been observed [210]. With increase in the degree of completion of the α + β transformation the yield stress increases from 65 to 165 MPa and the relative elongation changes from 21 to 5%. The strain-hardening is even larger for Nb-H system [211]. The specimen before hydrogenation is very ductile and shows an elongation by more than 30%. After the specimen being hydrogenated to a composition of Nb-30 at% H, the flow stress is greatly increased and fracture occurs after a little plastic deformation (total elongation less than 1%). The strain-hardening behavior can be expected in other metal-hydrogen systems where the metal is ductile.

The above analysis applies to the precipitation from an infinite matrix. The results are readily applied to the calculation of accommodation energy for hydride formation in a bulk metal where the precipitate is the hydride and the matrix is the metal. For hydride decomposition after the specimen is completely converted into the hydride, we can consider that metal precipitates from the hydride and then the precipitate is the metal, the matrix is the hydride and ε < 0. Thus the elastic and plastic accommodation energies for hydride formation have the same values as those for hydride decomposition only when the metal and the hydride have
identical elastic and plastic properties. The mechanical properties of metal hydrides are usually quite different from those of their parent metals. Metal hydrides are more brittle. Moreover, the mechanical properties of metal hydrides are different in compression and tension. Many of the hydrides exhibit some plastic deformation when tested in compression, particularly at a high temperature, but the response to a tensile stress has generally been a brittle fracture [212]. Therefore, elastic and plastic accommodation energies are generally not equal for hydride formation and hydride decomposition.

For metal-hydrogen systems where the metal is a fine powder, equations 5.1 to 5.13 should be modified to include an extra "image" elastic field coming from the free surface. This extra "image" elastic field is a hydrostatic pressure [213]

\[ \bar{P} = -16\pi \mu c / 3V \] (5.16)

where \( c \) is a constant measuring the strength of the precipitate and \( V \) is the volume of the specimen. When \( c > 0 \), \( c \) is positive and \( \bar{P} \) is a tension. For \( c < 0 \), \( \bar{P} \) is a compression.

By including the effect of \( \bar{P} \) which has an opposite sign to \( P \) we can see that stress components and accommodation energies are reduced due to the effect of free surface. The
reduction increases with the decrease of the specimen volume. When \( V \) is sufficiently small, the equivalent stress which is now given by

\[
\sigma_e = -\frac{3}{2} \left[ \frac{P}{r^3} + \frac{r}{P} \right] = -6\mu \left[ \frac{\beta c(a/r)^3 - 4\pi c/3V}{16} \right]
\]  

(5.17)

will be smaller than \( \sigma_y \). Then no plastic deformation will occur and the crystal remains in a purely elastic state.

In general, the relaxation of misfit strain through a free surface is possible whenever the interface between the precipitate and the matrix is close to the free surface. As a result, the transformation stress and accommodation energy are reduced. When a hydride is formed at or near a free surface, the hydride will be able to relieve much of its misfit strain by expansion normal to the surface. Even if a new phase is formed inside a bulk specimen the effect of the free surface can be expected when the new phase grows to a size comparable to that of the specimen.

The effect of the free surface on the accommodation energy of hydride formation was observed in Nb-H system using TEM [102]. On cooling hydrogen-charged foil samples the hydride was formed only in the thinnest portion around the central perforation, indicating that the accommodation energy there is the minimum. This surface effect was also seen in
the distribution of hydride precipitation sizes in a H/Nb = 0.1 foil quenched to 77 K. In the thinnest foil sections the hydride precipitate diameters were 4-5 μm while in foil regions of about 1000-2000 Å thickness the sizes were 1-2 μm.

The following conclusions can be drawn from the discussion in this section:

(1) Hydride formation and decomposition are accompanied by transformation stresses due to a volume change. When the transformation stresses exceed the yield strength plastic deformation occurs. This elastic and plastic accommodation depends not only on the misfit strain and the elastic and plastic properties of the metal and hydride but also on the sizes of the precipitate and the specimen.

(11) The elastic and plastic accommodation energies for hydride formation would equal those for hydride decomposition only when the metal and the hydride have identical elastic and plastic properties. Since hydrides are usually more brittle than host metals, elastic and plastic accommodation energies are generally not equal for hydride formation and hydride decomposition.

(111) In the early stage of precipitation, the effective yield stress becomes the theoretical yield strength and hence plastic relaxation is not possible unless the transformation stress is extremely large. When the precipitate grows to the size of the order of micron or above, the effective yield stress becomes a macroscopic yield stress.
(iv) For soft materials with an ideal plastic behavior, plastic accommodation effects will reduce the total accommodation energy to very small amounts and the plastic component of this energy dominates.

(v) For highly strain-hardening materials, plastic accommodation will reduce the total accommodation energy by only a small amount and most of this remaining energy will be in the form of elastic energy.

(vi) For brittle materials (most intermetallic compounds) the fracture strength will be exceeded with little or no plastic deformation and hence the elastic component will dominate the total accommodation energy.

(vii) The misfit strain of hydride formation and decomposition can be relaxed through a free surface, resulting a lower transformation stress and a decreased accommodation energy, when the specimen is a fine powder or very thin foil, when the new phase is formed at or near the free surface and when the new phase grows to a size comparable to that of the specimen. If the volume of a powder specimen is sufficiently small, no plastic deformation will occur and the host material remains in a purely elastic state.

5.4 Nucleation and Growth in Hydride Formation and Decomposition

The accommodation energy discussed in the previous
section, along with the interfacial energy, plays a vital role in the nucleation and, to a lesser degree, growth in hydride formation and decomposition.

According to the classical nucleation theory, i.e. that nucleation proceeds via a thermally activated critical clustering process, the free energy change for homogeneous nucleation in solid state phase transformation, $\Delta G^N$, when a new phase of volume $V$ and interface area $A$ forms, causing an increase in accommodation energy per mole of precipitate $\Delta G_{\text{accom}}$, is given as

$$\Delta G^N = V \left[ \frac{(\Delta G_{\text{chem}} + \Delta G_{\text{accom}})}{V} \right] + A\sigma \quad (5.18)$$

where $\Delta G_{\text{chem}}$ is the molar chemical free energy to form the nucleus from the parent phase, $V_m$ is the molar volume of the new phase, $\sigma$ is the specific interfacial energy. For a spherical embryo of radius $r$, Eq. 5.18 becomes

$$\Delta G^N = \frac{4}{3} \pi r^3 \left[ \frac{(\Delta G_{\text{chem}} + \Delta G_{\text{accom}})}{V_m} \right] + 4\pi r^2 \sigma \quad (5.19)$$

The chemical free energy and accommodation energy are both dependent on the volume. Only if $\Delta G_{\text{chem}}$ is larger (more negative) than $\Delta G_{\text{accom}}$, which is almost inevitably positive, will the reaction proceed. The volume of the nucleus increases as the third power of the nucleus size, while the area term, which is positive and acts as the barrier to the
process, increases only as the second power of the nucleus size. At small radii the nucleus is unstable and tends to redissolve in the matrix. Only when the precipitate has reached the critical radius, \( r^* \), and the critical free energy increases, \( \Delta G^* \), does the nucleus become capable of metastable existence, and after addition of one atom \( r > r^* \) it can grow with a continuous decrease of free energy. For a spherical nucleus the values of the critical parameters are given by

\[
r^* = -2\sigma / \left[ (\Delta G_{\text{chem}} + \Delta G_{\text{accom}}) / V \right]
\]

(5.20)

\[
(\Delta G^N)^* = \left( \frac{16}{3} \pi \sigma^3 \right) / \left[ (\Delta G_{\text{chem}} + \Delta G_{\text{accom}}) / V \right]^2
\]

(5.21)

The critical formation energy of a nucleus \( (\Delta G^N)^* \) is equal to one third of the critical interfacial energy and is supplied by the energy fluctuation in the matrix. The other two third of the critical interfacial energy must be provided by the increase of the driving force of the reaction, i.e. the chemical free energy being more negative. From Eq.5.20 we have

\[
\Delta G_{\text{chem}} = - \left( 2\sigma V / r^* + \Delta G_{\text{accom}} \right)
\]

(5.22)

Eq.5.22 represents the supersaturation which is required for nucleation. The nucleation rate \( I \) has an exponential
dependence on the critical formation energy \((\Delta G^N)^*\), which is given by

\[
I \propto \exp \left[ -\frac{(\Delta G^N)^*}{kT} \right]
\]  \hspace{1cm} (5.23)

Where \(k\) is Boltzmann constant and \(T\) is absolute temperature. At the low temperature of interest, the nucleation rate will be undetectably small if the absolute value of \(\Delta G_{\text{chem}}\) is only slightly larger than \(\Delta G_{\text{acc}}\).

In general, nucleation in hydride formation and decomposition is heterogeneous. Preferred precipitation of the hydride phase on the surface, grain boundaries and dislocations has been observed [84, 177, 214-218]. The energy barrier for heterogeneous nucleation is much smaller than that for homogeneous nucleation due to the reduction of the interfacial energy and/or the accommodation energy. The analysis for nucleation of incoherent precipitates on grain boundaries and on dislocations by Nicholson [219] and by Cahn [220, 221] shows that when the nucleus forms on the pre-existing defect the energy of formation of the nucleus is reduced by that proportion of the defect energy which is consumed by the nucleus as it is formed. For coherent precipitation on dislocations, the interaction energy between the elastic field of the dislocation and the elastic field produced by the misfit between matrix and precipitate is very important, and the energy barrier of nucleation is reduced.
and may even disappear due to this interaction energy [222]. Nucleation on surfaces will, in addition to the reduction in interfacial energy, greatly reduce the accommodation energy as discussed in the previous section.

The expressions for heterogeneous nucleation corresponding to Eqs. 5.18-5.23 are quite complex [219-222]. Nevertheless, Eqs. 5.18-5.23 can be modified qualitatively by simply adding an energy term to account for the effect of heterogeneous nucleation. Let $\Delta G_{\text{def}}^N$ be the contribution of defects to nucleation energy, i.e. the reduction of the accommodation energy and/or interfacial energy due to heterogeneous nucleation, then the molar nucleation energy can be written as

$$\Delta G^N = \Delta G_{\text{chem}} + \Delta G_{\text{accom}} + \Delta G_{\text{inter}} - \Delta G_{\text{def}}^N \quad (5.24)$$

Where $\Delta G_{\text{inter}}$ is the interfacial energy. For homogeneous nucleation $\Delta G_{\text{def}}^N$ is equal to zero while for heterogeneous nucleation it is a positive term, reducing the total nucleation energy. The magnitude of $\Delta G_{\text{def}}^N$ depends on the local concentration of defects.

The energy relationship described by Eq. 5.24 is also applicable to the growth of new phase in hydride formation and decomposition. However, the relative contributions to the total free energy change of the accommodation energy, the interfacial energy and the energy associated with the defects
are changed. At the nucleation stage, the new phase would be in a purely elastic state and hence

\[
\Delta G_{\text{accom}}^N = \Delta G_{e_1} = E_{e_1} V
\]  

(5.25)

Where \( E_{e_1} \) is given by Eq. 5.5. After nucleation, the new phase will grow to a size where plastic relaxation occurs and the accommodation energy is now composed of elastic and plastic components, i.e.

\[
\Delta G_{\text{accom}}^P = \Delta G_E + \Delta G_P = (W_E + W_P)V
\]  

(5.26)

where \( W_P \) and \( W_E \) are given by Eqs. 5.10 and 5.11 respectively. After sufficient growth the interfacial energy term is negligible compared with the energy terms associated with volume since the volume increases as the third power while the area increases only as the second power. The energy contribution due to defects in the growth of the new phase, which depends on the overall concentration of defects, is also relatively small and, in most cases, can be omitted. Hence, the molar free energy change in the growth of the new phase can be written as

\[
\Delta G^G = \Delta G_{\text{chem}} + \Delta G_E + \Delta G_P
\]  

(5.27)

The above discussion is based on the classical nucleation
theory. Such a theory may not be strictly applicable to the nucleation in hydride formation and decomposition. There has been some evidence indicating that the structural aspect of hydride formation is similar to a martensitic type of transformation involving a shear process. Bradbrook [223] first suggested that hydride formation in zirconium must be a martensitic transformation. Carpenter [224] subsequently showed how a dislocation mechanism could produce such a martensitic transformation for the $\gamma$ hydride in pure zirconium. Weatherly [225] studied hydride formation in zirconium using TEM and concluded that hydride formation for both $\gamma$ and $\delta$ hydride is a plane strain (martensitic) transformation involving significant shear. Similar arguments are made for hydride precipitation in vanadium and niobium [226, 227], in zirconium-niobium alloy [228] and in titanium [229].

Nucleation of martensitic transformation is generally considered to be non-thermally activated and hence the classical nucleation theory is no longer valid. Nevertheless, martensitic transformation is still a nucleation and growth process and the expression for free energy change for a martensitic transformation is the same as Eq. 5.24. The absolute value of the chemical free energy term must be larger than the sum of the remaining energy components in order for a martensitic transformation to proceed.
5.5 Plateau Pressures and Pressure Hysteresis

We have analyzed the activation energy for dissociative absorption or associative desorption of hydrogen, elastic and plastic accommodation energies and interfacial energy. Now we look at how these energy terms affect the plateau pressures and pressure hysteresis.

First we assume that the rate-controlling step in the formation of metal hydride by the reaction of gaseous hydrogen with metal (Eq. 1.1) is the nucleation and growth of the hydride phase. If there were no accommodation energy and interfacial energy involved in the reaction, the free energy change per mole of atomic hydrogen would be given by

\[ \Delta G = \Delta G^0 - \frac{1}{2}RT \ln P_{H_2} \]  

(5.28)

At equilibrium, \( \Delta G = 0 \), which implies that

\[ \Delta G^0 = \frac{1}{2}RT \ln P_{eq} \]  

(5.29)

Thus we have

\[ \Delta G = \frac{1}{2}RT \ln P_{eq} - \frac{1}{2}RT \ln P_{H_2} \]  

(5.30)

\( \Delta G \) is the thermodynamic driving force and the reaction proceeds forward when the hydrogen pressure, \( P_{H_2} \), is higher
than the equilibrium pressure, $P_{eq}$.

The accommodation energy and interfacial energy act against the formation of hydride. These energies must be supplied by increasing the driving force, i.e. increasing the hydrogen pressure. With the existence of the accommodation energy and interfacial energy, the free energy change given by Eq. 5.30 may be referred as molar chemical free energy change, $\Delta G_{chem}$ and the total molar free energy change can be written for hydride formation as

$$\Delta G_f = \Delta G_{chem,f} + \Delta G_{non-chem,f}$$  \hspace{1cm} (5.31)

where the subscript $f$ represents hydride formation, and

$$\Delta G_{chem,f} = \frac{1}{2} RT \ln P_{eq} - \frac{1}{2} RT \ln P_{H_2}$$  \hspace{1cm} (5.32)

$$\Delta G_{non-chem,f} = \Delta G_{accom,f} + \Delta G_{inter,f} - \Delta G_{def,f}$$  \hspace{1cm} (5.33)

$P_{eq}$ is the hypothetical equilibrium pressure, i.e. the equilibrium pressure which would be attained without the influence of the accommodation energy and/or interfacial energy. $\Delta G_f$ is the net driving force for hydride formation. Hydride forms only when $\Delta G_f$ is negative. As $\Delta G_f$ approaches zero the reaction stops. The hydrogen pressure obtained from Eq. 5.31 by letting $\Delta G_f = 0$ is the minimum value required for hydride formation to proceed.

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\[ \frac{1}{2} \text{RTln}P_{f,\text{ein}} = \frac{1}{2} \text{RTln}P_{\text{eq}} + \Delta G_{\text{non-chem},f} \]

\[ = \frac{1}{2} \text{RTln}P_{\text{eq}} + \Delta G_{\text{accom},f} + \Delta G_{\text{inter},f} - \Delta G_{\text{def},f} \]

(5.34)

By a similar argument we can obtain for hydride decomposition:

\[ \Delta G_d = \Delta G_{\text{chem},d} + \Delta G_{\text{non-chem},d} \]

\[ = -\frac{1}{2} \text{RTln}P_{\text{eq}} + \frac{1}{2} \text{RTln}P_{\text{eq}} + \Delta G_{\text{accom},d} + \Delta G_{\text{inter},d} - \Delta G_{\text{def},d} \]

(5.35)

\[ \frac{1}{2} \text{RTln}P_{\text{d,max}} = \frac{1}{2} \text{RTln}P_{\text{eq}} - \Delta G_{\text{non-chem},d} \]

\[ = \frac{1}{2} \text{RTln}P_{\text{eq}} - \Delta G_{\text{accom},d} - \Delta G_{\text{inter},d} + \Delta G_{\text{def},d} \]

(5.36)

Where the subscript \(d\) represents hydride decomposition, \(P_d\) is the maximum hydrogen pressure allowed for hydride decomposition to proceed.

If there were no non-chemical free energy terms, the reaction would proceed reversibly at \(P_{H_2} = P_{\text{eq}}\). The
existence of the accommodation energy and interfacial energy makes the reaction proceed irreversibly at $P_{H_2} \geq P_{f,\text{min}}$ for hydride formation and at $P_{H_2} \leq P_{d,\text{max}}$ for hydride decomposition, resulting in pressure hysteresis which, in general, can then be expressed by

$$\frac{1}{2} RT \ln P_f/P_d = \Delta G_{\text{non-chem}, f} + \Delta G_{\text{non-chem}, d}$$ (5.37)

Where the non-chemical free energy terms depend on various experimental conditions.

For a complete hydriding and dehydriding cycle, the hydride formation is by nucleation and growth of the hydride phase and the entire specimen is converted into hydride during hydriding; during dehydriding, the hydride decomposition is by nucleation and growth of the metal phase and the entire specimen is converted into the original metal. The accommodation energy at the nucleation stage is given by Eq. 5.25 and at the growth stage (after plastic deformation) by Eq. 5.26. The interfacial energy and the energy contribution of defects are important to nucleation energy but they may generally be neglected during the growth of the new phase. Thus we have for hydride formation

$$\frac{1}{2} RT \ln P_f^{N} = \frac{1}{2} RT \ln P_{eq} + \Delta G_{\text{el}, f} + \Delta G_{\text{inter}, f} - \Delta G_{\text{def}, f}$$
\[
\frac{1}{2} \text{RTlnP}^G_{e,q,f} = \frac{1}{2} \text{RTlnP}^G_{e,q} + \Delta G_{e,f} + \Delta G_{p,f}
\]

\[
= \frac{1}{2} \text{RTlnP}^G_{e,q} + \left( W_{e,f} + W_{p,f} \right) V^H_{\text{HH}} \tag{5.39}
\]

And for hydride decomposition

\[
\frac{1}{2} \text{RTlnP}^N_{d,m,n} = \frac{1}{2} \text{RTlnP}^N_{e,q} - \Delta G_{e,d} - \Delta G_{p,d} + \Delta G_{\text{def},d}
\]

\[
= \frac{1}{2} \text{RTlnP}^N_{e,q} - \left( W_{e,d} + W_{p,d} \right) V^H_{\text{HH}} \tag{5.40}
\]

\[
\frac{1}{2} \text{RTlnP}^G_{d,m,n} = \frac{1}{2} \text{RTlnP}^G_{e,q} - \Delta G_{e,d} - \Delta G_{p,d}
\]

\[
= \frac{1}{2} \text{RTlnP}^G_{e,q} + \left( W_{e,d} + W_{p,d} \right) V^H_{\text{HH}} \tag{5.41}
\]

Where the superscript N represents nucleation, G represents growth; \( V_{\text{HH}} \) and \( V^H_{\text{HH}} \) are molar volume of the metal hydride phase and the metal phase respectively. It should be pointed out that after a complete phase transformation there is stored in the specimen only residual elastic strain energy which is composed of that due to non-uniform deformation and
that stored in dislocations and other defects. The interfacial energy and the majority of the elastic strain energy created during phase transformation are converted into heat as the reaction fraction approaches unity. The residual elastic strain energy is small compared with the total accommodation energy and hence can be neglected. Therefore the accommodation energy and interfacial energy are irreversible in a complete hydride formation and decomposition cycle and they must be supplied by increasing the driving force for each phase transformation, i.e. by increasing the hydrogen pressure for hydride formation and by decreasing the hydrogen pressure for hydride decomposition.

During the first few hydride formation and decomposition cycles intermetallic compounds will disintegrate into a fine powder with a mean particle size being about 10 μm while most pure metals and alloys will retain their bulk form. The plateau pressures will change during the first few cycles and then remain virtually constant. Here we first consider this constant plateau pressure and leave the effect of cycling to be discussed later in this section.

In the determination of PC isotherms of a bulk specimen, the hydride phase will begin to nucleate when \( P_{H_2} = P_{f, min} \), after doses (aliquots) of hydrogen are added into the reactor containing a fully dehydrided specimen. The hydriding reaction continues with the growth of the nucleated hydride when more hydrogen is added. For each aliquot of hydrogen
added, the hydride grows until \( P_{H_2} = P_{f, \text{min}}^G \). Therefore the measured time-invariant hydrogen pressure for hydride formation at the nucleation stage, \( P_f^N \), is equal to \( P_{f, \text{min}}^N \) and that for the growing hydride, \( P_f^G \) is equal to \( P_{f, \text{min}}^G \). A similar argument applies to dehydriding process so that

\[
\begin{align*}
  P_f^N &= P_{f, \text{min}}^N \\
  P_f^G &= P_{f, \text{min}}^G \\
  P_d^N &= P_{d, \text{max}}^N \\
  P_d^G &= P_{d, \text{max}}^G
\end{align*}
\]  

(5.42)  

(5.43)  

(5.44)  

(5.55)

The magnitude of pressure hysteresis is usually evaluated at the mid-point of the pressure plateaus where the pressure is determined by \( P_f^G \) or \( P_d^G \), i.e.

\[
\frac{1}{2} RT \ln \frac{P_f}{P_d} = \frac{1}{2} RT \ln \frac{P_f^G}{P_d^G}
\]  

(5.46)

Thus the pressure hysteresis for a bulk specimen is

\[
\begin{align*}
  \frac{1}{2} RT \ln \frac{P_f}{P_d} &= \frac{1}{2} RT \ln \frac{P_f^G}{P_d^G} \\
  &= \Delta G_{E,f} + \Delta G_{P,f} + \Delta G_{E,d} + \Delta G_{P,d}
\end{align*}
\]  

(5.47)
In most cases the energy barrier for nucleation is larger than that for growth, i.e.

\[ P^N_{r,\text{min}} > P^G_{r,\text{min}} \]  \hspace{1cm} (5.48)

\[ P^N_{d,\text{max}} < P^G_{d,\text{max}} \]  \hspace{1cm} (5.49)

For a bulk specimen

\[ P^N_r > P^G_r \]  \hspace{1cm} (5.50)

\[ P^N_d < P^G_d \]  \hspace{1cm} (5.51)

This effect of nucleation energy has been observed [129] in the recently determined, very precise PC isotherms of the Pd-D\(_2\) system. At the beginning of the absorption branch (left-hand side) the pressure displays a small maximum and at the beginning of the desorption branch (right-hand side) a small minimum. If the PC isotherms are measured with large aliquot size this nucleation effect may not be observed.

A powder specimen usually consists of an enormous number of tiny particles. Each particle must undergo its own nucleation and growth process. Once a particle is nucleated the whole particle will soon be converted into the new phase so that a partially hydried specimen consists of fully hydried particles and non-hydrided particles. In this case
the measured time-invariant hydrogen pressure depends on the aliquot size employed in the measurement. With a certain reactor volume the aliquot size is determined by the initial hydrogen pressure, $P_{H_2}^0$ and the final time-invariant hydrogen pressure, $P_f$ or $P_d$. Consider two extreme cases:

(i) very small aliquot size, $P_{H_2}^0$ is only slightly larger than $P_{f,\text{min}}^N$. The nucleation rate is very low. Imagine only one particle is nucleated. The growth of the supercritical nucleus will transform the whole particle into hydride, but only cause a very small change in reaction fraction and hydrogen pressure. If the hydrogen pressure $P_{H_2}^f$ is still larger than $P_{f,\text{min}}^N$, another particle may be nucleated and then converted into the new phase, again causing a very small change in hydrogen pressure. This process may repeat until $P_{H_2}^f = P_{f,\text{min}}^N$, then the reaction is at an apparent equilibrium. Thus the time-invariant hydrogen pressure for a powder specimen measured with very small aliquot sizes is given by

$$P_f^s = P_{f,\text{min}}^N$$

(5.52)

where the superscript $s$ represents small aliquot.

(ii) Very large aliquot size. $P_{H_2}^0 \approx P_{f,\text{min}}^N$. The nucleation rate is very high so that a large number of particles are nucleated for each aliquot of hydrogen added.
The nuclei in these particles will grow until the hydrogen pressure drops to \( P_{f, \text{min}}^G \). Hence the time-invariant hydrogen pressure for a powder specimen measured with very large aliquot sizes is given by

\[
P^I_f = P^G_{f, \text{min}}
\]

(5.53)

where the superscript \( I \) represents large aliquot. Similar arguments apply to the hydride decomposition process and we have

\[
P^s_d = P^N_{d, \text{max}}
\]

(5.54)

\[
P^l_d = P^G_{d, \text{max}}
\]

(5.55)

Then the pressure hysteresis for a powder specimen determined by very small aliquot sizes can be written as

\[
\frac{1}{2} RT \ln \frac{P^s_f}{P^s_d} = \frac{1}{2} RT \ln \frac{P^N_{f, \text{min}}}{P^N_{d, \text{max}}}
\]

\[
= \Delta G_{\text{el}, f} + \Delta G_{\text{el}, d} + \Delta G_{\text{inter}, f} + \Delta G_{\text{inter}, d}
\]

\[- \Delta G_{\text{def}, f} - \Delta G_{\text{def}, d}
\]

(5.56)

That determined by very large aliquot sizes can be written as
\[ \frac{1}{2} \text{RT} \ln \frac{P_f}{P_d} = \frac{1}{2} \text{RT} \ln \frac{P^G_{E, \text{min}}}{P^G_{E, \text{max}}} \]

\[ = \Delta G_{E, f} + \Delta G_{P, f} + \Delta G_{E, d} + \Delta G_{P, d} \quad (5.57) \]

The effect of aliquot size on the plateau pressure for hydride formation can be expressed by

\[ \frac{1}{2} \text{RT} \ln \frac{P^R}{P_f} = \Delta G_{E, f} + \Delta G_{\text{int}, f} - \Delta G_{\text{def}, f} \quad (5.58) \]

and for hydride decomposition

\[ \frac{1}{2} \text{RT} \ln \frac{P^R}{P_d} = \Delta G_{E, d} + \Delta G_{\text{int}, d} - \Delta G_{\text{def}, d} \quad (5.59) \]

From Eqs. 5.48 and 5.49, and Eqs. 5.56 and 5.57 we see that the pressure hysteresis for a powder specimen measured by small aliquot sizes is larger than that measured by large aliquot sizes.

Eqs. 5.52-5.59 represent the maximum effect of aliquot size. The experimentally measured pressure hysteresis employing small aliquot size will be smaller than but close to the value given by Eq.5.56 and that employing large aliquot size will be larger than, but close to, the value given by Eq.5.57. This would explain the experimental observation [56] that there seem to be limiting values for
the effect of large aliquot size on the reduction of hysteresis. In general, the experimentally determined (with a certain value of aliquot size) time-invariant plateau pressure for hydride formation of powder samples lies between the value given by Eq. 5.52 and 5.53

$$P_{f, \text{min}}^G < P_f < P_{f, \text{min}}^N$$  \hspace{1cm} (5.60)

and that for hydride decomposition lies between the value given by Eq. 5.54 and 5.55

$$P_{d, \text{max}}^N < P_d < P_{d, \text{max}}^G$$  \hspace{1cm} (5.61)

Thus the plateau pressures of powder samples are controlled by a combined effect of the energy barrier for nucleation ($\Delta G_{el} + \Delta G_{\text{inter}} - \Delta G_{\text{def}}$) and that for growth ($\Delta G_e + \Delta G_f$). With a certain aliquot size an increase of the energy barrier for nucleation would result in an increase of $P_f$ or a decrease of $P_d$.

No research work has been reported on the effect of aliquot size on the pressure hysteresis for bulk samples. We suggest that the aliquot size may affect the pressure hysteresis for a bulk specimen if the phase transformation proceeds by nucleation and growth of the new phase in each individual grain or domain.

In conclusion, elastic strain energies as well as plastic
energies in both hydride formation and decomposition will contribute to pressure hysteresis for bulk samples. The pressure hysteresis for powder samples varies with aliquot size and is determined by a combined effect of the energy barrier for nucleation, which is built up by elastic strain energy in the purely elastic state and the interfacial energy, and the energy barrier for growth, which is created by elastic and plastic energy in the elasto-plastic state. In the extreme case of very small aliquot size, pressure hysteresis for powder samples results from elastic strain energies and interfacial energies in both hydride formation and decomposition while plastic energy makes no contribution.

Based on the above analysis most experimental observations on the plateau pressures and pressure hysteresis can be readily explained, namely:

(1) Effect of temperature and composition

All the energy components which may contribute to hysteresis are affected by temperature and the composition of the host materials. The accommodation energy depends on the shear modulus (Eq. 5.5 and 5.12). The decrease of the shear modulus with temperature may be the main reason for the decrease of hysteresis with increase in temperature.

The elastic and plastic properties of metals are generally not a linear function of the composition so that hysteresis may vary dramatically with the variation of the composition of host metals.
(11) Effect of particle size

The hydride formation and decomposition in bulk samples takes place under more severely constrained condition than those in powder samples. A powder sample can release some of phase transformation strain through free surfaces. An extra "image" elastic field coming from the free surface is a hydrostatic pressure (Eq. 6.16) which is inversely proportional to the volume of the specimen. This hydrostatic pressure reduces the accommodation energy. Thus hysteresis is larger for bulk samples than for finely divided samples.

(iii) Effect of hydriding/dehydriding cycling and surface contamination

The variation of plateau pressures and hysteresis with effect of hydride formation and decomposition cycling during the first few cycles, we suggest, may result from: (1) a decrease of particle size (2) an increase of dislocations and other defects and (3) the creation of uncontaminated surface. The decrease of particle size will reduce hysteresis as we already discussed. The increase of dislocations and other defects will influence the nucleation energy. Heterogeneous nucleation at dislocations and other defects may greatly reduce the accommodation energy and interfacial energy, resulting in a lower energy barrier for nucleation so that the plateau pressures decrease for hydride formation and increase for hydride decomposition. Therefore hysteresis is reduced.
It is our belief that the most important change occurring during the first few cycles is the change of surface condition of the specimen. An enormously large clean surface is created upon hydrogenation, whereas the surface of virgin specimen is contaminated by adsorption of small amount of impurities or the formation of surface layers such as oxides. As discussed in Section 5.2 the energy barrier for the dissociative absorption or associative desorption of hydrogen in clean hydride forming metals is non-existent or very small, whereas the surface contamination can create a large energy barrier or greatly increase it. This energy barrier, which is assumed to be negligible in deriving Eqs. 5.31-5.61, could be much larger than that for nucleation and growth. To overcome this energy barrier hydrogen chemical potential must be increased. In this case, the experimentally determined plateau pressures for hydride formation can be expressed by

\[
\frac{1}{2} RT \ln P_f = \frac{1}{2} RT \ln P_{eq} + \Delta G_{abs} \quad (5.62)
\]

and for hydride decomposition

\[
\frac{1}{2} RT \ln P_d = \frac{1}{2} RT \ln P_{eq} - \Delta G_{des} \quad (5.63)
\]

where \( \Delta G_{abs} \) and \( \Delta G_{des} \) are energy barriers for the dissociative absorption or associative desorption of hydrogen. Therefore, when \( \Delta G_{abs} \) and \( \Delta G_{des} \) are larger than the energy barrier for
nucleation and growth due to significant surface contamination, the plateau pressures for hydride formation increase and those for hydride decomposition decrease. The plateau pressures are determined by the energy barrier for the surface process rather than by the energy barrier for nucleation and growth so that the particle size and the density of defects will not affect the plateau pressures.

It can be expected that $G_{abs}$ and $G_{des}$ will be larger for the first cycle than those for subsequent cycles and in the first cycle $G_{abs}$ will be larger than $G_{des}$. If the original surface of the specimen is severely contaminated, $G_{abs}$ for the first cycle will be much larger than those for subsequent cycles and much larger than $G_{des}$ for the first cycle. This explains the experimentally observed variation of plateau pressures of LaNi$_5$ hydride during the first three cycles (Fig.4.8): the hydride formation pressure for the first cycle is much higher than those for further cycles whereas the hydride decomposition pressure does not change very much. The surface contamination of Zr(Fe$_x$Cr$_{1-x}$)$_2$ samples is less severe than that of LaNi$_5$ since Zr(Fe$_x$Cr$_{1-x}$)$_2$ samples are much more easily activated than LaNi$_5$. Thus the effect of cycling for Zr(Fe$_x$Cr$_{1-x}$)$_2$ (Fig.4.9-4.11) is less pronounced than that for LaNi$_5$. After the first few cycles, the exact number of cycles depending on the specific metal-hydrogen systems, the energy barrier for surface process becomes smaller than that for nucleation and growth and then the plateau pressures
are determined by the energy barrier for nucleation and growth and they remain constant since both the densities of defects and the particle have saturated at this stage. Thus we propose that the effect of cycling on plateau pressures and hysteresis during the first few cycles is largely due to the change in surface condition of the specimen which affects the energy barriers for dissociative absorption and associative desorption of hydrogen. Our experimental results (see Section 4.6) that the plateau pressure for hydride formation increases after the specimen is exposed to air and the longer exposure time the higher the plateau pressure support the above argument.

(iv) Effect of annealing

There are two possible reasons for the effect of annealing on the plateau pressures for hydride formation. First, the vacuum annealing of fully dehydrided samples reduces the densities of dislocations and other defects, causing a reduction of $\Delta G_{\text{def}}$ and hence resulting in a higher nucleation energy, which, in turn, leads to an increased hydride formation pressure. Second, the sample surface may be oxidized during annealing due to an imperfect vacuum, thus setting up a larger energy barrier for chemisorption of hydrogen and resulting in a higher hydride formation pressure.

The available experimental results suggest that the surface contamination rather than the reduction of defect
density is responsible for the effect of annealing. The hydride formation pressure of \( \text{LaNi}_5 \) has been found to increase dramatically following annealing (Fig.2.5) [57]. The effect of \( \Delta G_{\text{def}} \) is expected to be relatively small whereas the effect of \( \Delta G_{\text{abs}} \) could be very large. It has also been observed [59] that annealing of fully dehydrided \( \text{LaCo}_5 \), in contrast to the behavior of \( \text{LaNi}_5 \), does not significantly affect the hydride formation pressure. The reduction of defect concentration due to annealing should be similar for both \( \text{LaNi}_5 \) and \( \text{LaCo}_5 \) but the extent of surface contamination could be quite different. \( \text{LaCo}_5 \) is much easier to activate than \( \text{LaNi}_5 \), which implies that \( \text{LaNi}_5 \) is more liable to surface contamination.

5.6 Sloping plateaus and smooth corners at the ends of a plateau.

These phenomena are more apparent in intermetallic compounds-hydrogen systems. Intermetallic compounds disintegrate into fine powders upon hydrogenation. The plateau pressures for powder samples are affected by the nucleation energy (Eqs. 5.60 and 5.61). The energy barrier for nucleation is composed of three components: \( \Delta G_{\text{el}} + \Delta G_{\text{inter}} - \Delta G_{\text{def}} \). Different particles have different sizes and different densities of defects, resulting in a distribution of the values of the energy barrier for nucleation, which, in turn, leads to the sloping plateaus.
and the smooth change of hydrogen pressure at the ends of a plateau. The plateau pressures for bulk samples is determined by $P_{f,min}^N$ or $P_{d,min}^N$ at the nucleation stage and by $P_{f,min}^G$ or $P_{d,max}^G$ at the growth stage. Different nucleation sites may have different values of energy barrier for nucleation, resulting in variation of $P_{f,min}^N$ or $P_{d,max}^N$, which, in turn, causes the smooth changes of hydrogen pressure at the beginning of plateaus. The accommodation energy at the growth stage depends on the flow stress. Because of strain-hardening the flow stress increases as phase transformation proceeds, resulting in sloping plateaus.

For both powder and bulk samples, if the composition of the host material is inhomogeneous, there will be a distribution of the values of $P_{eq}$ among different portions of the specimen, causing the sloping plateau and smooth corners at the ends of a plateau.

5.7 Thermal Hysteresis

Thermal hysteresis is closely related to pressure hysteresis. All the factors contributing to pressure hysteresis may also affect thermal hysteresis (In this section $\Delta G_{del}$ is, for convenience, combined into $\Delta G_{accom}$ and $\Delta G_{inter}$, so that $\Delta G_{non-chem} = \Delta G_{accom} + \Delta G_{inter}$). Nevertheless, the real physical situations corresponding to pressure hysteresis and thermal hysteresis are, in some aspects, quite different. In the case of thermal hysteresis,
only a small fraction of the specimen undergoes a phase transformation instead of the whole specimen, and the specimen remains in a bulk form. The elastic strain energy and interfacial energy created during hydride precipitation are stored in the specimen and will aid the reverse phase transformation, i.e. they are reversible.

When a dilute solid solution of hydrogen is cooled down, hydride will precipitate from the solid solution and this process is accompanied by elastic and, when the internal stress exceeds the yield stress, plastic accommodation. The strain energy must be supplied by increasing the driving force, i.e. by lowering the temperature below the equilibrium, or stress free terminal solid solubility. At the early stage of precipitation when the size of the precipitate is smaller than 1 μm the specimen remains in a purely elastic state and the accommodation energy is $E_{el}$, given by Eq. 1. If the temperature of the specimen is reversed at this stage, the precipitate will dissolve into the solid solution and the stored elastic energy, which is generated during hydride precipitation, will contribute to the driving force for the reverse transformation, allowing it to occur "prematurely". Thus there will be an equal decrease in the transformation temperature on heating and on cooling and no hysteresis will be observed. In this case, the elastic strain energy and interfacial energy will not contribute to hysteresis. In fact, the interfacial energy will not contribute to thermal
hysteresis in any case since the interfacial energy produced
during hydride precipitation is removed by hydride
dissolution and the total interfacial energy change is zero.
The elastic strain energy, however, will generally contribute
to thermal hysteresis (see below).

In most practical situations the precipitate is able to
grow to a sufficiently large size and plastic relaxation will
occur. The accommodation energy for the growing hydride is
the sum of elastic and plastic energy, i.e.

\[ G_{\text{accom,p}} \text{(growing)} = \Delta G_{P,p} + \Delta G_{E,p} \]  \hspace{1cm} (5.64)

where the subscript p represents hydride precipitation. When
the temperature of the specimen is reversed, the stored
elastic energy will assist the dissolution of the hydride,
just as in the case where the specimen remains in a purely
elastic state. But with the progress of the dissolution, the
elastic stress associated with elastic strain due to the
volume expansion during hydride precipitation will reverse
its sign because of the volume decrease during hydride
dissolution, and when the yield stress is exceeded plastic
defformation again takes place. The accommodation energy for
the dissolving hydride is

\[ \Delta G_{\text{accom,d}} \text{(dissolving)} = \Delta G_{P,d} + \Delta G_{E,d} \]  \hspace{1cm} (5.65)
where the subscript \( d \) represents hydride dissolution. The elastic and plastic accommodation energies for both growing and dissolving hydrides must be supplied by increasing the driving force for each phase transformation, i.e. by lowering the temperature for hydride precipitation or by increasing the temperature for hydride dissolution. Thus the thermal hysteresis between the growing and dissolving hydrides reflects the total elastic and plastic accommodation energies in both hydride precipitation and dissolution.

In general, thermal hysteresis is a reflection of the total accommodation energy in hydride precipitation and dissolution. The magnitude of the thermal hysteresis is usually expressed by

\[
\frac{\Delta T}{T_p} = \frac{T_d - T_p}{T_p}
\]

(5.66)

Where \( T_p \) is the hydride precipitation temperature and \( T_d \) is the hydride dissolution temperature. For hydride precipitation we have

\[
\frac{1}{2} R T_p \ln P_{H_2} = \frac{1}{2} R T_p \ln P_{eq} (at T_p) + \Delta G_{non-chem, p}
\]

(5.67)

and for hydride dissolution

\[
\frac{1}{2} R T_d \ln P_{H_2} = \frac{1}{2} R T_d \ln P_{eq} (at T_d) + \Delta G_{non-chem, d}
\]

(5.68)

Where \( P_{H_2} \) is the hydrogen pressure corresponding to the
overall hydrogen concentration in the specimen at which hydride precipitation and dissolution take place, and $P_{eq}$ is the hydrogen pressure corresponding to the hypothetical equilibrium solvus concentration at a given temperature. From Eqs. 5.67 - 5.68, and by employing the Van't Hoff equation

$$\frac{d\ln K}{dT} = \frac{-\Delta H}{RT^2}$$  \hspace{1cm} (5.69)

We may deduce

$$\Delta T \frac{|\Delta H|}{T_p} = \Delta G_{\text{non-chem, p}} + \Delta G_{\text{non-chem, d}} + \Delta G_{\text{non-chem, p}} / T_p$$  \hspace{1cm} (5.70)

Where $\Delta H_{eq}$ is assumed to be independent on temperature. Since the magnitude of $T_p$ is in the order of several hundred K the last term in Eq. 5.70 may be omitted and then we have

$$\Delta T \frac{|\Delta H|}{T_p} = \Delta G_{\text{non-chem, p}} + \Delta G_{\text{non-chem, d}}$$  \hspace{1cm} (5.71)

$$= \Delta G_{\text{accom, p}} + \Delta G_{\text{inter, p}} + \Delta G_{\text{accom, d}} + \Delta G_{\text{inter, d}}$$

In the case of thermal hysteresis, $\Delta G_{\text{inter, d}} = -\Delta G_{\text{inter, p}}$, then the above equation becomes

$$\Delta T \frac{|\Delta H|}{T_p} = \Delta G_{\text{accom, p}} + \Delta G_{\text{accom, d}}$$  \hspace{1cm} (5.72)
or
\[ \frac{\Delta T}{T_p} \propto \Delta G_{\text{accom},p} + \Delta G_{\text{accom},d} \]  \hspace{1cm} (5.73)

Therefore the thermal hysteresis between the growing and dissolving hydrides can be expressed by

\[ \frac{\Delta T}{T_p} \text{(growing and dissolving)} \propto \Delta G_{p,p} + \Delta G_{e,p} + \Delta G_{p,d} + \Delta G_{e,d} \]  \hspace{1cm} (5.74)

If the experimental technique employed is sensitive enough the temperature for hydride nucleation and/or the onset of the hydride dissolution may be detected. The accommodation energy for hydride nucleation is

\[ \Delta G_{\text{accom},p} \text{ (nucleation)} = \Delta G_{el} \]  \hspace{1cm} (5.75)

and that at the onset of the hydride dissolution after the hydride grows to a sufficiently large size so that plastic relaxation takes place is

\[ \Delta G_{\text{accom},d} \text{ (onset of dissolution)} = -\Delta G_{e,p} \]  \hspace{1cm} (5.76)

where \( \Delta G_{e,p} \) is the elastic strain energy stored in the specimen during the growth of hydride. This stored energy will aid the reverse transformation in its early stage. From Eqs. 5.64, 5.65, 5.73, 5.75, 5.76 we can describe the thermal hysteresis determined at hydride nucleation and the onset of
the hydride dissolution as

\[ \Delta T/T_p (\text{nucleation and onset of dissolution}) \propto \Delta G_{el} - \Delta G_{E,p} \]  
(5.77)

The thermal hysteresis determined at hydride nucleation and dissolving hydride is

\[ \Delta T/T_p (\text{nucleation and dissolving}) \propto \Delta G_{el} + \Delta G_{P,d} + \Delta G_{E,d} \]  
(5.78)

And the thermal hysteresis determined at growing hydride and the onset of hydride dissolution is

\[ \Delta T/T_p (\text{growing and onset of dissolution}) \propto \Delta G_{P,p} \]  
(5.79)

It is clear that in most cases the elastic accommodation energy will contribute to thermal hysteresis even if this energy is reversible in the situations associated with thermal hysteresis. On the other hand, the plastic accommodation energy in hydride precipitation, which is irreversible, does not contribute to the thermal hysteresis determined at hydride nucleation and the onset of the hydride dissolution, and that determined at hydride nucleation and dissolving hydride.
Fig. 5.1 Potential energy curves for activated and non-activated chemisorption of hydrogen on a clean metal surface and endothermic or exothermic solution in the bulk [178].
Fig. 5.2 Transformation stress as a function of hydrogen concentration in metals: (a) ideal plastic behavior; (b) significant strain-hardening; (c) brittle materials.
Fig. 5.3 Schematic of the plastic zone surrounding a misfitting spherical precipitate [206].
CHAPTER 6
SUMMARY AND SUGGESTED FUTURE RESEARCH

\[ \text{Zr(Fe}_{x} \text{Cr}_{1-x})_{2} \text{ hydrides exhibit pronounced hysteresis over} \]

the temperature range from 283.2 to 353.2K. The degree of hysteresis decreases with increasing temperature and increases with increasing iron substitution for chromium. The hysteresis factors, \( \frac{1}{2}RT\ln P_f/P_a' \), range from 217 J/mol H for \( x = 0.5 \) at 343.2K to 1169 J/mol H for \( x = 0.8 \) at 283.2K. The magnitude of hysteresis determined with large aliquots is smaller than that determined with small aliquots. Hysteresis is also reduced during the first few cycles of hydride formation and decomposition. The effects of aliquot size and cycling are quite small compared with those of \( \text{LaNi}_5 \) hydride.

Significant sloping plateau behaviors are observed for \( \text{Zr(Fe}_{x} \text{Cr}_{1-x})_{2} \) hydrides. There is no apparent dependence of the plateau slopes on temperature and the composition of parent metals for hydride formation while the plateau slopes for hydride decomposition seem to increase with increasing temperature and Fe content. The plateau slopes, \( d(\ln P)/(H/M) \), for hydride formation are about 0.9 and those for hydride decomposition range from 0.5 to 1.1. Similar to hysteresis, the plateau slopes decrease with cycling during the first few cycles. The same phenomenon is also observed for \( \text{LaNi}_5 \) hydride.
The subsequent plateau pressure for hydride formation and its slope increase after a fully dehydrated sample is exposed to air. The longer the sample is exposed to air, the higher the plateau pressure and the larger the plateau slope. The sample can be fully recovered with virtually the same absorption PC isotherm as that before exposure to air by cycling in ultrahigh-purity hydrogen. These experimental results suggest that the surface contamination affects the plateau pressures, hysteresis and sloping plateaus.

The experimental observations in this investigation and in other publications indicate that hysteresis and sloping plateau pressures in metal-hydrogen systems are quite complex. Not only do many experimental variables affect hysteresis, including temperature, composition, aliquot size, cycling, annealing, particle size and surface contamination, but also one particular variable may affect hysteresis in a different manner in different systems. The existing theoretical models seem not to be adequate to explain the complete range of experimentally observed behavior. These models can be generally divided into two groups. In the first group, the origin of hysteresis is believed to be a strain effect in hydride formation. The desorption branches of the hysteresis loop of a PC isotherm are considered to represent the true strain-free equilibrium whereas the absorption branches represent, instead, an equilibrium under mechanical constraints. In the second group of models, it is argued that
hysteresis results from the free energy dissipation due to plastic deformation during both hydride formation and decomposition and elastic strain energy will not contribute to hysteresis.

To determine the nature and origin(s) of hysteresis and sloping plateau pressures in metal-hydrogen systems, it is necessary first to have a clear picture of the physical situations associated with hydride formation and decomposition. Hydride formation or hydride decomposition consists of a sequence of elementary steps. Among these steps dissociative absorption or associative desorption, and nucleation and growth are fundamentally more important, especially when one deals with the time-independent phenomena of hysteresis and sloping plateaus. The energy barrier for the dissociative absorption or associative desorption of hydrogen in clean transition metals and probably many other metals (alloys and intermetallic compounds) which form metal hydrides is non-existent or very small whereas the surface contamination may create a large energy barrier or greatly increase it. Due to this large energy barrier, the reaction rate can be negligibly small at low temperatures or the reaction may be totally blocked if this energy is not supplied externally by the increase of hydrogen chemical potential. Both hydride formation and hydride decomposition are accompanied by elastic and plastic strains. The elastic and plastic accommodation depends not only on the misfit
strain and the mechanical properties of the metals and hydrides, but also on the sizes of the new phase and the specimen. In both hydride formation and hydride decomposition, the accommodation energy and the interfacial energy build up an energy barrier for nucleation and growth. These energies must be provided by increasing the driving force, i.e., by increasing the hydrogen pressure for hydride formation or by decreasing hydrogen pressure for hydride decomposition. Hysteresis thus results. It is incorrect to assume that the strain effect only exists during hydride formation as in the "strain" models. It is also incorrect to exclude the effect of elastic accommodation as in the "plastic deformation" models.

A close examination of the accommodation energy and its effect on the experimentally determined time-invariable plateau pressures leads to the expressions for plateau pressures and hysteresis. The pressure hysteresis for well activated bulk samples results from elastic strain as well as plastic deformation during both hydride formation and decomposition. The pressure hysteresis for well activated powder samples (most intermetallic compounds, including Zr(Fe$_{x}$Cr$_{1-x}$)$_{2}$ and LaNi$_{5}$) varies with aliquot size and is determined by a combined effect of the energy barrier for nucleation, which is built up by elastic strain energy in the purely elastic state and the interfacial energy, and the energy barrier for growth, which is created by elastic and
plastic energy in the elasto-plastic state. In the extreme case of very small aliquot size, pressure hysteresis for powder samples results from elastic strain energies and interfacial energies in both hydride formation and decomposition while plastic energy makes no contribution.

The relative contributions of elastic or plastic energies to the total accommodation energy depend mainly on the mechanical properties of the metal and the hydride. For soft materials with ideal plastic behavior, the elastic component of the total accommodation energy after plastic relaxation is very small and hence may be neglected. In this case plastic accommodation energy is the major cause of hysteresis, and McKinnon’s (29) assumption that the internal stresses are completely relaxed by plastic deformation is approximately valid. For highly strain-hardening materials and brittle materials, however, the elastic component dominates the total accommodation energy and the contribution of the plastic energy can be neglected. Therefore the conclusion drawn by Sinha and Wallace (38) is appropriate for these materials, i.e. that hysteresis is primarily a consequence of the elastic strain energy.

The pressure hysteresis for samples with contaminated surfaces is probably determined by the energy barrier for surface process. Thus the effects of cycling and annealing are largely due to the change of surface condition of the sample. Other factors which affect hysteresis are also
readily explained.

The sloping plateaus and the smooth change of hydrogen pressure at the ends of plateaus, for samples with homogeneous composition, may be caused by the variation of the values of the energy barrier for nucleation or growth among different particles (powder sample) or different portions (bulk sample) of the sample.

Thermal hysteresis is not influenced by interfacial energy. The contribution of elastic and plastic accommodation energies to thermal hysteresis depends on how the magnitude of thermal hysteresis is determined experimentally. In most cases the elastic accommodation energy will contribute to thermal hysteresis even if this energy is reversible in the situations associated with thermal hysteresis. On the other hand, the plastic accommodation energy in hydride precipitation, which is irreversible, does not contribute to the thermal hysteresis determined at hydride nucleation and the onset of the hydride dissolution, and that determined at hydride nucleation and dissolving hydride.

The present model allows correct qualitative and semiquantitative explanations for hysteresis and sloping plateaus in metal-hydrogen systems. The quantitative calculation of hysteresis and sloping plateaus is not possible at present because of the lack of knowledge about the mechanical properties of metal hydrides and intermetallic compounds which form hydrides. Furthermore, the analytical
expressions for accommodation energy involves an assumption of a spherical precipitate morphology which may not be strictly valid for hydrides. The explanation for the effect of cycling and annealing is tentative since only quite limited experimental work has been performed regarding these effects. More research, both theoretical and experimental, needs to be done to fully understand the plateau pressures, hysteresis and sloping plateaus in metal-hydrogen systems.

The following research work is suggested:

(i) Continue the investigation of the effects of surface condition and lattice strain on plateau pressures, hysteresis and sloping plateaus. Study the surface properties of \( \text{Zr(Fe,Cr}_{x,1-x,2} \) intermetallic compounds with Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Determine the degree of surface oxidation and the lattice strain change due to annealing of the dehydried sample at different temperatures, and compare the results with the corresponding PC isotherms.

(ii) Measure the PC isotherms for pure metals (e.g., Pd, Nb, V) - H systems with various hydrogen aliquot sizes to see whether aliquot size has an effect on plateau pressures and hysteresis on these systems.

(iii) Determine the elastic and plastic properties of \( \text{Zr(Fe,Cr}_{x,1-x,2} \) intermetallic compounds (and other hydride forming materials) and their hydrides. Modify the theoretical model for calculation of accommodation energies to take into
account the morphology of hydrides and then calculate the 
elastic and plastic energies and compare them with the 
experimentally determined magnitude of hysteresis and plateau 
slopes.

(iv) Measure PC isotherms dynamically, i.e. with a 
constant hydrogen flow rate of a given value. Dynamic PC 
isotherms are properties directly related to the performance 
and efficiency of metal hydride heat pumps and other metal 
hydride energy conversion systems. Hysteresis increases when 
measured dynamically. The dynamic hysteresis is influenced by 
an effect similar to aliquot size, and the increase of 
dynamic hysteresis is also due to kinetic factors. A certain 
value of the driving force, i.e. \( P_{H_2} - P_{c} \) or \( P_{d} - P_{H_2} \) is 
necessary to maintain a certain reaction rate, which may be 
controlled by any intrinsic elementary step or by heat 
transfer and/or mass transfer. It is recommended first to 
measure the PC isotherms with a controlled hydrogen flow rate 
for each aliquot of hydrogen; then determine the PC isotherms 
continuously with a constant hydrogen flow rate using a very 
small amount of sample to eliminate the effect of heat and/or 
mass transfer; finally build a prototype metal hydride heat 
pump or other metal hydride energy conversion systems and to 
investigate the effect of hysteresis and sloping plateaus on 
the performance and efficiency of the unit. The measurement 
of dynamic PC isotherms would require some modification of 
the experimental apparatus.
APPENDIX

Graphical Separation of Profiles Obtained Using $K_\alpha$

X-radiation: Rachinger Correction [153, 154]

The Rachinger correction assumes that the intensity of the $\alpha_2$ component is half that of the $\alpha_1$ component so that the contribution of $\alpha_2$ towards a diffraction line has the same shape as that of $\alpha_1$ except that it is half the height and shifted towards larger angles by

$$\Delta(2\theta) = 2 \tan \theta \Delta \lambda / \lambda$$

where $\Delta \lambda = \lambda(\alpha_2) - \lambda(\alpha_1)$ and $\lambda$ is the weighted mean wavelength of the doublet

$$\lambda = [\lambda(\alpha_2) + \lambda(\alpha_1)]/3$$

The principle of the Rachinger separation is illustrated in Fig. A1.

Fig. A1(a) represents the individual contributions of $\alpha_1$ and $\alpha_2$ to the total diffraction profile shown in Fig. A1(b). These contributions are identical in shape except for a 2:1 ratio in intensities and a shift of $\Delta(2\theta)$ corresponding to wavelength difference.

Ordinates are drawn on the experimental curve as shown in Fig. A1(b) starting at the low-angle end of the profile where the intensity is assumed zero. These are spaced at intervals of $\Delta(2\theta)/m$, where $m$ is integral, the choice being determined
to give an adequate number of points. If \( I_1 \) is the ordinate at position \( i \) and \( I_1(\alpha_1) \) is the contribution of \( \alpha_1 \) alone then

\[
I_1(\alpha_1) = I_1 - I_1(\alpha_2) = I_1 - 1/2 \cdot I_{1-m}(\alpha_1)
\]

The intervals in Fig. A1(b) correspond to \( m=3 \) and the values for \( I_1(\alpha_1) \) for \( m = 1, 2 \) and 3 is listed in Table A1.

The values of \( I_1(\alpha_1) \) are readily evaluated by starting from the low angle end of the profile and accuracy is reasonable across about halfway down the high-angle side of the curve. Beyond this region, accuracy is low since small differences between two nearly equal quantities are involved and smoothing of the fluctuations in the calculated values may be necessary.

The process is illustrated in Fig. A1(c) which is drawn for intervals of \( \Delta(2\theta)/3 \). The half-heights of \( I_1(\alpha_1) \) are transposed by \( \Delta(2\theta) \) to higher angles to form the intensities for \( I(\alpha_2) \) at the positions \( 1+3 \). These values of \( I_{1+3}(\alpha_2) \) are then subtracted from the total observed curve \( I(\alpha_1) + I(\alpha_2) \) at positions \( 1+3 \) to give \( I_{1+3}(\alpha_1) \). Thus the curves for \( I(\alpha_1) \) and \( I(\alpha_2) \) may be drawn through the ordinates so derived.
### Table A1 Values for $I_m(\alpha_1)$ for $m = 1, 2$ and $3$

<table>
<thead>
<tr>
<th>$m$</th>
<th>$I_1(\alpha_1)$</th>
<th>$I_2(\alpha_1)$</th>
<th>$I_3(\alpha_1)$</th>
<th>$I_4(\alpha_1)$</th>
<th>$I_5(\alpha_1)$</th>
<th>$I_6(\alpha_1)$</th>
<th>$I_7(\alpha_1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0$</td>
<td>$I_1$</td>
<td>$I_3 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_4 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_5 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_6 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_7 - \frac{1}{2} I_1(\alpha_1)$</td>
</tr>
<tr>
<td>2</td>
<td>$0$</td>
<td>$I_1$</td>
<td>$I_3 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_4 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_5 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_6 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_7 - \frac{1}{2} I_1(\alpha_1)$</td>
</tr>
<tr>
<td>3</td>
<td>$0$</td>
<td>$I_1$</td>
<td>$I_3 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_4 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_5 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_6 - \frac{1}{2} I_1(\alpha_1)$</td>
<td>$I_7 - \frac{1}{2} I_1(\alpha_1)$</td>
</tr>
</tbody>
</table>
Fig. A1 Principle of the Rachinger separation of profiles obtained using $K_\alpha$ X-radiation.
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