



Studies about Interaction of Hydrogen Isotopes with Metals and Intermetallic Compounds

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ABSTRACT

Hydrogen is a non-toxic but highly inflammable gas. Compared to other inflammable gases, its range of inflammability in air is much broader (4-74.5%) but it also vaporizes much more easily. Handling of hydrogen in form of hydrides enhances safety.

The interaction of hydrogen with metals and intermetallic compounds is a major field within physical chemistry.

Using hydride-forming metals and intermetallic compounds, for example, recovery, purification and storage of heavy isotopes in tritium containing system can solve many problems arising in the nuclear-fuel cycle.

The paper presents the thermodynamics and the kinetics between hydrogen and metal or intermetallic compounds.

1 INTRODUCTION

Interactions between hydrogen isotopes and metals or intermetallic compounds are important from applied and fundamental science point of view. These systems offer, for example, the possibility of technical hydrogen isotopes separation and a lot a problems of hydrogen recovery, hydrogen purification and tritium storage can be resolved.

The continuous contamination of heavy water from the Nuclear Power Plant Cernavoda equipped with a Canadian reactor, reduces the moderator's efficiency. For these reasons, ICIS Rm. Valcea has developed a detritiation technology, based on catalytic isotopic exchange and cryogenic distillation. Tritium should be removed from the tritiated heavy water, and this will necessitate the storage of tritium in a special vessel that can provide a high level of protection and safety of environment and personal.

The storage of hydrogen isotopes as metal hydrides is considered a safe and modern technique.

2 KINETICS AND THERMODYNAMICS FOR THE INTERACTION BETWEEN HYDROGEN ISOTOPES AND METALS OR INTERMETALLIC COMPOUNDS

The nature and the extent of hydrogen isotopes interactions with materials are due to the physical, chemical and nuclear properties to the initial position of hydrogen in the periodic table. The characteristic transport and reactivity properties are evident in the large class of systems where hydrogen is highly mobile solute element in many metals.

2.1 Thermodynamics interactions

The metal hydrides produced according to the reaction [1]:



A pressure, composition, and temperature diagram commonly and most conveniently represents the behaviour of a metal-hydrogen system. An idealized diagram of this type, which can be regarded as a special type of phase diagram, is shown in Figure 1 [2].

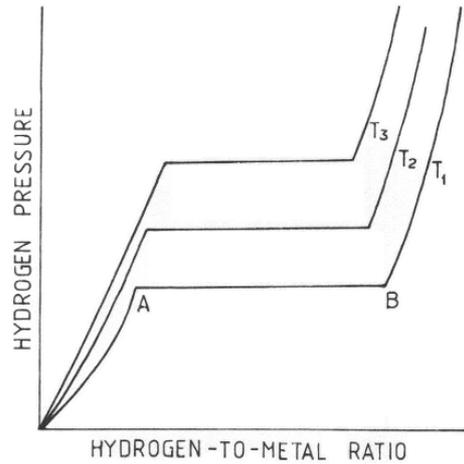


Figure 1: Ideal pressure-temperature-composition diagram

It consists of a family of isotherms, which shows the variation of the equilibrium pressure with the concentration of hydrogen in the solid. At a given temperature, hydrogen will dissolve in the metal phase as the pressure increases. This single-phase region is usually designated as the α phase of the hydrogen-metal system. Ideal, the isotherm in any single solid phase region will obey Sievert's law, which states that the concentration of hydrogen in the solid phase is proportional to the square root of the equilibrium pressure, P .

$$\text{Conc. } H_{\text{solid}} = KP^{1/2} \quad (2)$$

Thermodynamic quantities regarding the formation of a metal hydride can be derived from the variation of equilibrium pressure with temperature by means of the van't Hoff reaction isobar (eq. 3), which defines the equilibrium constant (K) in terms of the heat of reaction (H) and the temperature (T).

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2} \quad (3)$$

For reaction (1),

$$K = \frac{a_{MH_x}}{a_M f_{H_2}^{x/2}} \quad (4)$$

At low pressures, the fugacity (f) may be considered equal to the pressure (P) and, since both solids are considered pure phases, their activities (a) may taken as unity.

Then,

$$K = \frac{1}{P_{H_2}^{x/2}} = P_{H_2}^{-x/2} \quad (5)$$

Specifying ΔH as a constant (which is usually true over a reasonable temperature range), equation (3) can be rewritten as:

$$d \ln P_{H_2}^{-x/2} = \frac{\Delta H}{RT^2} dT \quad (6)$$

Which upon integration yields:

$$\ln P_{H_2} = \frac{2\Delta H}{XRT} + C \quad (7)$$

If the hydride is stoichiometric and the solubility of hydrogen is small in the original metal, the standard enthalpy of formation (ΔH_f^0) can be derived from the slope of the straight line obtained by plotting $\ln P$ against $1/T$. Equation 7 is commonly presented in the form $\ln P_{H_2} = (A/T)+B$, where the constants A and B are specified.

Under these conditions, the standard free energy of formation can also be readily calculated. The free energy change in any reaction can be determined by:

$$\Delta G = \Delta G_f^0 + RT \ln K \quad (8)$$

At equilibrium:

$$\Delta G = 0 \quad (9)$$

thus:

$$\Delta G_f^0 = -RT \ln K \quad (10)$$

which, for reaction (1) upon substituting for K, yields

$$\Delta G_f^0 = \frac{x}{2} RT \ln P_{H_2} \quad (11)$$

Finally, the standard entropy of formation can be found by the equation [3]:

$$\Delta S_f^0 = \frac{\Delta H_f^0 - \Delta G_f^0}{T} \quad (12)$$

In systems which are appreciably nonstoichiometric, the standard enthalpy of formation of the hydride will be the sum of three components: the integral heat of solution of

hydrogen in the α phase from zero hydrogen content to saturation, the heat of reaction is going from the hydrogen saturated α phase to the pure but nonstoichiometric hydride β phase, and the integral heat of solution of hydrogen in the hydrogen-deficient β phase to the specified stoichiometric value. This procedure also is valid for ΔG_f^0 and ΔS_f^0 . However, in cases where large deviations from stoichiometry occur, thermodynamic values are more conveniently obtained and are usually expressed as relative partial molar quantities ($X_H - 1/2 X_{H_2}^0$), where X_H is the partial molar enthalpy (entropy or free energy) of hydrogen (as atoms) in the solid and $X_{H_2}^0$ refers to hydrogen in its standard state as a pure, diatomic, ideal gas. In order to obtain integral quantities, the partial molar quantities may be integrated over the entire composition range from the pure metal to the stoichiometric composition [2].

2.2 Kinetics

Most reports in the literature begin by considering the complexity of the process, which transforms a molecule in the gas phase into a bound atom in the lattice of the final solid product. This process is classically divided into a sequence of elementary steps consisting of gas transport, surface adsorption and dissociation, transition from surface to bulk, diffusion, nucleation and growth. The main objective of kinetics is the identification of the slowest mechanism, or other words of rate-determining step. It is assumed that only one of the above steps has the rate slow enough, compared to the others, to control the reaction. In addition, the heat and mass transport are minimal and therefore not regulating steps.

Hydriding reaction kinetics can be treated considering the special characteristics of the metal / hydride systems that contribute significantly to make the interpretation of the kinetics very complicated. These characteristics are exothermic formation, fast reaction rates even near ambient temperature, and poor thermal conductivity of the hydride phase and embrittlement of products. The system appears to be very sensitive to small changes both in the surface or bulk morphology and in their purity of the solid and gaseous phases.

The importance of kinetic studies on hydride/H₂ system lies in the fact that kinetics appears to be one of the fundamental factors determining if the storing system is of the interest in practical applications. The major aim of kinetic study is to identify the regulating steps and to find ways to speed up the kinetics.

As an example of one simple one-dimensional model, the heat balance equation can be represented as

$$C_p \rho \frac{T}{t} = \lambda \frac{\partial^2 T}{\partial L^2} - r \rho \Delta H \quad (13)$$

where C_p is the specific heat capacity, ρ the density, T the absolute temperature, t is time, λ is the thermal conductivity, L is the distance, ΔH is the reaction enthalpy and r is the rate constant as a function of temperature, pressure and reacted fraction [4].

During the calculation, the simulation results are fitted to the experimental results; successive improvements can then be made to the rate equation and the model used to describe the metal hydride bed.

3 CONCLUSIONS

This paper present theoretical aspects of the interactions of hydrogen with metals and intermetallic compounds and contain information about thermodynamic and kinetics. Storage of hydrogen isotopes as metal hydride is recognized as most compact, suitable and safe method. The properties of metal hydrides suitable for hydrogen storage include the ability to bind isotopes strongly at normal temperature and pressure, and being easily prepared. The next paper will be present a comparative study between hydrogen absorption in titanium powder and titanium sponge.

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