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# New model of phase equilibria in metal – hydrogen systems: Features and software

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## ARTICLE INFO

### Article history:

Received 12 October 2015

Received in revised form

6 December 2015

Accepted 6 December 2015

Available online xxx

### Keywords:

Metal hydrides

Thermodynamics

PCT diagram

Modelling

## ABSTRACT

A new semi-empirical model of phase equilibria of hydride forming metals and alloys with hydrogen gas (PCT diagrams) has been developed. Within the model, pressure – composition isotherms (PCI's) for hydrogen absorption and desorption are presented as pseudo-convolutions of one core function, or “ideal” PCI built according to Lacher model, or model of Van der Waals lattice gas, with two modified asymmetric pseudo Voight distribution functions. The median of the absorption distribution is shifted from the one of the desorption distribution towards higher pressures, by the value related to a minimum of a hysteresis free energy (assumed to be constant) and an excessive chemical potential of hydrogen in over-saturated  $\alpha$ -solid solution.

The model allows to simultaneously fit both  $H_2$  absorption and desorption datasets and adequately simulates the features of experimental PCT diagrams in wide temperature range including (i) presence of several plateau segments, (ii) hysteresis including its disappearance when approaching to critical temperature, (iii) shape of transitions between  $\alpha$ -, ( $\alpha + \beta$ )- and  $\beta$ -regions, and (iv) flat or sloping plateaux including temperature and concentration dependencies of the plateau slope.

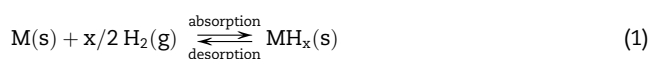
The article also presents a demonstration software (macro-enabled Excel workbook with an ActiveX calculation module) for the fitting of experimental PCT datasets verified on the systems  $H_2 - LaNi_{5-x}Sn_x$ ,  $H_2 - TiFe$  and  $H_2 - bcc-V(Ti,M)$ ;  $M = Zr, Ni$ .

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## Introduction

For gas phase applications of metal hydrides (MH) including hydrogen storage, hydrogen compression and heat management [1–5], the most important properties of hydride forming metals and alloys are their hydrogen absorption/desorption

capacities, as well as pressure – temperature conditions which correspond to the equilibrium of the reversible reaction:



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<http://dx.doi.org/10.1016/j.ijhydene.2015.12.055>

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Nomenclature			
$a$	maximum H filling fraction in $\alpha$ -phase	Y	generic fitting parameter
$a'$	maximum H filling fraction in over-saturated $\alpha$ -phase	z	ratio of critical and actual temperatures
$a^*$	attraction constant, Pa·m <sup>6</sup>	<i>Indexes</i>	
A	asymmetry	A	absorption
$b$	minimum H filling fraction in $\beta$ -phase	calc	calculated
$b'$	minimum H filling fraction in under-saturated $\beta$ -phase	C	critical
$b^*$	repulsion constant, m <sup>3</sup>	D	desorption
C	hydrogen concentration in the solid, H/M	exp	experimental
$d$	generic distribution parameter	g	gas
F	concentration- and temperature-dependent term of hydrogen equilibrium pressure	G	Gaussian
$f$	fugacity, atm	H	hydrogen atom
G	Gaussian distribution function	h	hysteresis
G	Gibbs free energy, J mol <sup>-1</sup>	i	number of plateau segment
H	enthalpy, J mol <sup>-1</sup>	I	interstitial
$h$	hysteresis energy loss, J mol <sup>-1</sup>	L	Lorentzian
$h_1$	coefficient of concentration dependence of enthalpy of hydrogen atoms in the solid, J mol <sup>-1</sup>	M	metal atom
$k$	Boltzmann constant (J K <sup>-1</sup> ), total number of plateau segments	max	maximum (asymptotic)
L	Lacher function	min	minimum
$m$	mixing factor	o	standard state
M	mixing coefficient	s	solid
N	number of atoms, number of experimental points	SH	entropy–enthalpy
P	pressure, Pa, atm	V	pseudo-Voight
$p$	ratio of actual and critical pressures	<i>Greek symbols</i>	
R	Universal gas constant, J mol <sup>-1</sup> K <sup>-1</sup>	$\alpha, \alpha'$	H solid solution phase
$R_f$	goodness of fitting	$\beta$	hydride phase
S	entropy, J mol <sup>-1</sup> K <sup>-1</sup>	$\delta$	delta function
s	slope factor	$\delta$	distance of experimental point from the calculated curve
SR	total squared deviation	$\phi$	fugacity coefficient
T	temperature, K	$\eta$	contribution of Lorentz profile
t	ratio of actual and critical temperatures	$\mu$	chemical potential, J mol <sup>-1</sup>
v	ratio of actual and critical volumes	$\theta$	filling fraction for ideal PCI
V	molar volume, m <sup>3</sup> mol <sup>-1</sup>	$\Theta$	filling fraction for non-ideal PCI
V	Van der Waals lattice gas function	$\rho$	Pearson correlation coefficient
w	width parameter	$\sigma$	standard deviation
W	segment weight	$\Omega$	specific matrix volume per a metal atom, m <sup>3</sup>
X	difference of logarithms of equilibrium and plateau pressures	$\psi$	distribution density
		$\Psi$	distribution integral
		$\Phi$	Concentration- and temperature-dependent term of hydrogen equilibrium pressure

where M is the hydride forming metal (alloy, intermetallic compound), the indexes s and g are related to the solid and gas phases, respectively.

Equilibrium of reaction (1) implies a unambiguous interrelation between gas pressure, P, hydrogen concentration in the solid, C, and temperature, T.

$$P = P(C, T), \text{ or } C = C(P, T) \quad (2)$$

The corresponding analytical or numerical dependence (PCT diagram) has to be derived using this or that modelling approach.

Engineering calculations of MH reactors based on the modelling of heat-and-mass transfer in the MH beds use, as a

rule, formal-empirical approach to the PCT modelling, by an arbitrary selection of a dependence which is more or less adequate to the experimentally observed behaviour (see, e.g. Refs. [6–12]). This approach is convenient for the applications, but unsatisfactory from the phenomenological point of view. Moreover, it often fails when the extrapolation out of the available experimental PCT limits is necessary.

PCT modelling based on statistical and / or thermodynamic prerequisites has a number of advantages including physical interpretability of coefficients in the corresponding analytical expressions (model fitting parameters) that enables to analyse the data for various materials, for example, with the purpose of their optimal integration in the application. It enables the

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