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Mathematical model of metal-hydride hydrogen tank with quick sorption

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ABSTRACT

In the paper we present a model of the hydrogen tank based on hydride-forming alloy powder with quick sorption. In this case we have the heat-controlling hydriding with spatial concentration redistribution. We construct the discrete model convenient for describing different shapes of tanks and configurations of cooling systems and for parallel calculating.

1. Introduction

Understanding the hydriding kinetics of metal powder particles in detail is very important for energy storage applications. An important problem is to develop a compact, light, and safe storage of hydrogen for mobile applications (including cars) [1,2]. Hydride tanks seem to be safer compared to high-pressure tanks due to lower gas pressure and self-cooling during desorption.

An obvious problem is to dissipate heat while loading the tank by hydrogen. Quick loading (2.5 min for 5 kg by 2015 according to the USA DOE objectives) and rather high heat of hydriding of most alloys result in significant power to be dissipated. E.g. an alloy with relatively low heat of hydriding 20 kJ/mol produces about 300 kW.

Heat released in hydride's bulk needs to be passed to cooled walls ("cooler" in the sequel). But evaluating heat fluxes in powder materials is also a problem, because their heat conductivity depends on porosity. For metal hydrides particles' size and therefore heat conductivity depend on the extent of hydriding. As no information is available about heat conductivity in metal hydride–hydrogen, we assume that the heat conductivity is constant.

Interesting effects appear due to hydrogen concentration redistribution between more and less cooled domains of the tank after the initial inflow of gas, when concentration of the sorbed hydrogen is in the binary phase area. They are especially noticeable in case of very high rates of hydrogen sorption and desorption, so that metal–hydride system is constantly in equilibrium with the surrounding hydrogen gas. Parts of hydride near cooled walls loose heat and sorb hydrogen to restore the equilibrium; the pressure goes down so other parts of hydride desorb some hydrogen and partly restore the decrease of pressure. Later the inverse process takes place: distant (with respect to cooled walls) parts of hydride are cooled by heat conductivity and sorb hydrogen, so earlier saturated parts desorb to compensate the decrease of pressure.

For modelling the tank we chose the Laves phase hydride $(Ti_{0.9}Zr_{0.1})_{1.1}CrMn$. P–C–T diagrams for this alloy [3] are in Fig. 1. The isotherms were constructed by linear interpolation of the points taken out from [3]. It has rather high rates of sorption–desorption. There are papers devoted to modelling of hydride tanks in detail [4,5]. Our aim is to create a simple model to represent interesting and basic effects that take place in tanks. This model can later be tuned for different materials and experimental conditions by more detailed description of necessary phenomena. Also the model will be used for comparing different configurations of coolers and studying nonlinear effects (like concentration redistribution mentioned above); such effects are important in real tanks but often are difficult to study at complex models and in experiments.

2. The mathematical model

We divide the bulk of the alloy in the two-phase area to N elementary cells with numbers i; the boundary of a cell consists of a few faces with number j. Two cells either have a common face, or have zero intersection. Cells need not to be rectangular and their faces need not to be flat. Let a cell's volume and its faces' areas be δ_i, S_i^j respectively. The concentration $c_i(t)$ and the temperature $T_i(t)$

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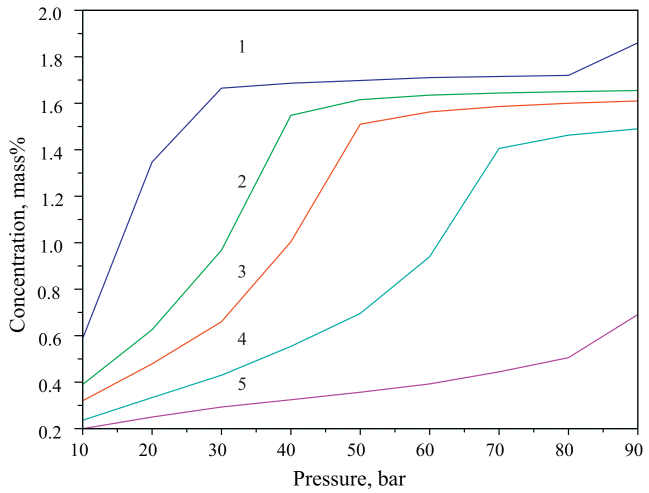

Fig. 1. Isotherms [3] for 0, 22, 32, 50, 80 °C (1–5 respectively).

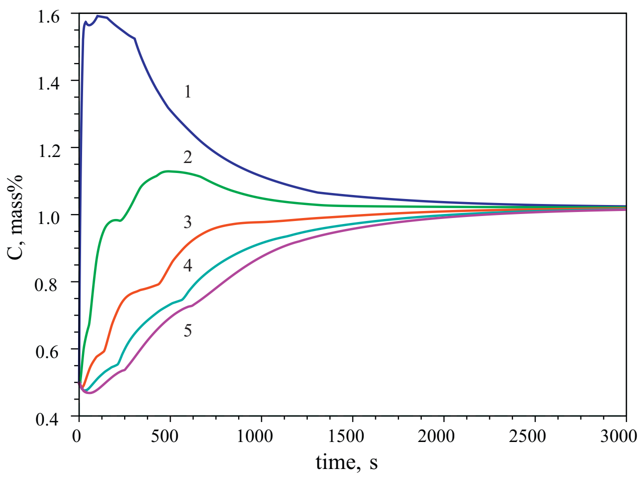

Fig. 2. Concentration in cells 1, 3, 5, 7, 9 (curves 1–5 respectively), 1d-model.

inside the i-th cell are considered to be spatially constant (average). The gas pressure, the same for all cells, is denoted by $P(t)$.

Due to equilibrium the quantities $P(t)$, $T_i(t)$, and $c_i(t)$ are not independent: the point (P, c_i) must lie on the isotherm for the given T_i. The ideal isotherms have a special plateau for the two-phase area, so that the concentration can be different for the same P and T_i; but the real isotherms (see Fig. 1) do not have the strict plateau, so the function $\bar{c}(P, T)$ is defined uniquely. Here we get the first model equation:

$$c_i = \bar{c}(P, T_i).$$

The initial values $P(0) = P_0$, $T_i(0) = T_i^0$, $c_i(0) = c_i^0$ are known; they are also not independent. As the initial content of hydrogen is given, we determine the temperatures T_i^0 from the equations $c_i^0 = \bar{c}(P_0, T_i^0)$ (using the same isotherms).

Another model equation follows from the general conservation law and the equation of gas state in the tank. We used the van der Waals equation, though the model can work with any:

$$\left(P + \frac{\alpha A^2}{V^2}\right)\left(\frac{V}{A} - \beta\right) = R\tilde{T}; \qquad (1)$$

here $\tilde{T}$ is the absolute temperature in the tank, A is the amount of hydrogen (moles) in gas, $\alpha = 2.484 \times 10^{10}\,\mathrm{Pa\,cm^6/mol^2}$ and $\beta = 26.635\,\mathrm{cm^3/mol}$ are the van der Waals quantities, V is the known tank's volume. The amount of hydrogen in gas due to conservation is

$$A = A(t) = A_0 - \sum_{i=1}^{N}\left(c_i - c_i^0\right)\delta_i. \qquad (2)$$

The gas temperature $\tilde{T}$ is assumed to be constant. Expressing the pressure we have $P(t) = \bar{P}(A)$.

To derive equations for T_i we need to describe the heat fluxes via cells' faces. A face can be either a boundary face (i.e. the common face of two cells), or a part of a cooled wall, or a part of a heat-isolated wall. In the first case let the heat flux density be

$$H_i^j = \frac{a}{d_i^j}(T_i - T_m), \qquad (3)$$

where a is the heat conductivity, d_i^j is the distance between the cells' centres, m is the index of the neighbour cell. This is the Fourier law. In the second case we use the linear expression:

$$H_i^j = K(T_i - T^*), \qquad (4)$$

where K is the cooling constant and T^* is the cooler's temperature. Heat-isolated walls are considered as coolers with $K = 0$. Note that the model can work with other cooling laws.

Heat conservation provides equations for T_i. Assume that volumetric heat capacity of the alloy is constant and unity. Temperature in a cell can change due to heat fluxes via faces and phase change only. Heat flux densities via each face are given by Eqs. (3) and (4), areas S_i^j of faces are known. Also some heat can be released or sorbed due to phase change in the cell, i.e. due to changing of $\bar{c}$: this heat is $\kappa d\bar{c}(P, T_i)$ where κ is the hydriding heat per a mole of hydrogen. Expressing $d\bar{c}$ via increments of pressure and temperature and writing down the conservation law, we get the equation

$$\left(1 - \kappa\frac{\partial \bar{c}}{\partial T}\right)\delta_i\frac{dT_i}{dt} = -\sum_j H_i^j S_i^j + \kappa\frac{\partial \bar{c}}{\partial P}\delta_i\dot{P}. \qquad (5)$$

Differentiating (1) with respect to t using (2) and the chain rule we have one more equation:

$$\left(1 + \frac{d\bar{P}}{dA}\sum_{i=1}^{N}\frac{\partial \bar{c}}{\partial P}\delta_i\right)\frac{dP}{dt}(t) = -\frac{d\bar{P}}{dA}\sum_{i=1}^{N}\frac{\partial \bar{c}}{\partial T}\delta_i\dot{T}_i. \qquad (6)$$

Now we have $N+1$ linear algebraic Eqs. (5), (6) for $N+1$ unknowns: $\dot{T}_i$ and $\dot{P}$. Note that this system has a special structure: its matrix is diagonal except a line and a column. Solving this system we get the nonlinear system of differential equations.

This model is convenient for describing different shapes of tanks and configurations of cooling systems: curved cells of different size and form can approximate any shape. Also the model can be effectively calculated using parallel computers.

3. Results and discussion

Let us first consider the simplest case of a symmetric tank: e.g. a sphere with cooled surface or a cylinder with cooled wall. Then the model can be reduced to a single spatial dimension. To illustrate the redistribution effect we considered 10 cells. Length of each cell is 2 cm. Alloy parameters (divided on unity heat capacity) were: $\kappa = 144$ K/mass %, $a = 0.9\,\mathrm{cm^2/s}$; cooler parameters: $K = 1$ cm/s, $T^* = 290$ K; tank parameters: $\tilde{T} = 300$ K, $P_0 = 60$ bar, $V = 1$ L. In order to solve the gas state equation, we need the cross-section of cells; it was $30\,\mathrm{cm^2}$. Initial concentration was 0.5 mass%. In Fig. 2 there are concentrations in cells numbered 1, 3, 5, 7, and 9 beginning from the nearest to the cooler. Concentration redistribution effect is clearly seen: for about a minute the most distant cell desorbs, while the cooled cell quickly sorbs hydrogen; later the cooled cell

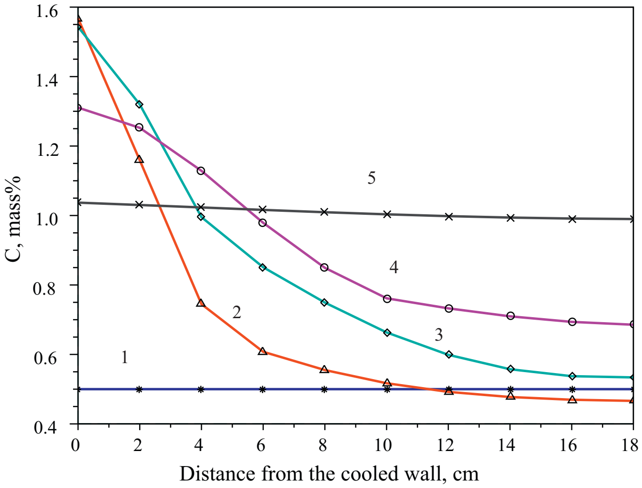

Fig. 3. Concentration distribution at a few times, 1d-model. Asterisks (1), triangles (2), diamonds (3), circles (4), and crosses (5) correspond to 0, 70, 250, 500, and 2000 s respectively.

gives hydrogen back, while the distant cells take it. In the end an even distribution is obtained. This can also be seen in Fig. 3, where the concentration distribution at different times is shown. Temperatures, being initially the same, become different due to cooling, but in the end all cells are cooled down to the cooler's temperature (Fig. 4).

To illustrate the ability of the model to describe complex configurations we consider a cylinder (cross-section radius 2.5 cm, length 16 cm, other parameters were the same as in the previous example) with three cooling pipes parallel to the cylinder's axis situated at half-radius and at equal angles. In this case the model is reduced to two dimensions convinient for presenting figures. The cylinder cross section is divided into 12 concentric rings of equal radial thickness and 36 equal angle sectors (10° each). This is an example of non-equal cell structure with curved faces. The cooler pipes were assumed to occupy a cell each. In Figs. 5 and 6, there are the consentration distributions in the beginning of the experiment and after half the time has passed. Cooler pipes are white in the pictures. One can see that difference between the most and the least saturated domains becomes slightly less and the distributuion in general becomes more even (e.g. least saturated area is less and middle-concentration area is larger). Due to more effective cooler and smaller size of the tank (0.6 L vs. 0.1 L), the time is significantly reduced (100 s of full saturation vs. 3000 s in one-dimensional case).

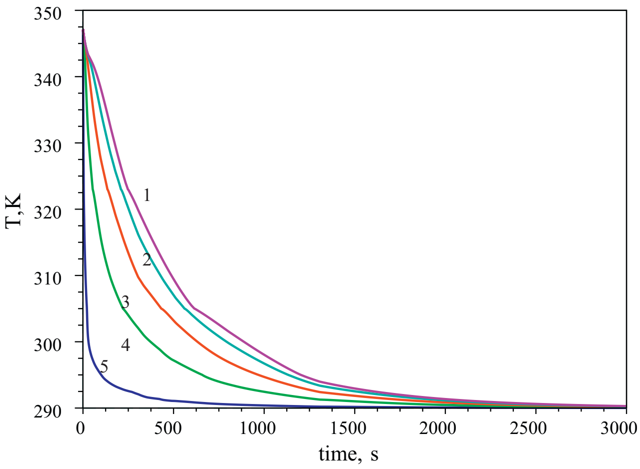

Fig. 4. Temperature in cells 1, 3, 5, 7, 9 (curves 1–5 respectively), 1d-model.

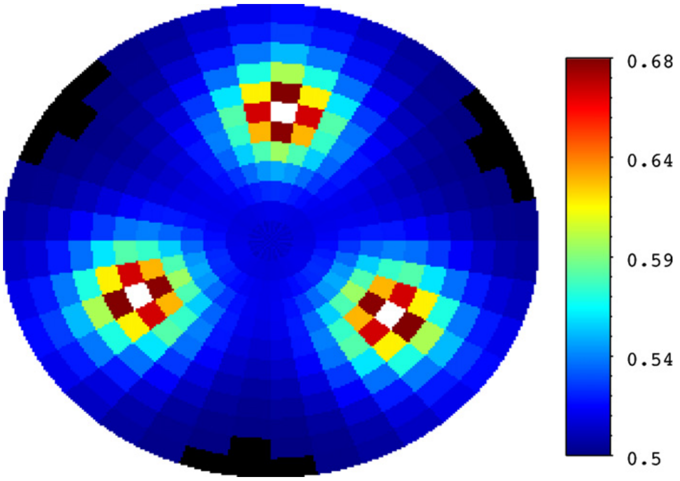

Fig. 5. Concentration distribution, 2d-model, 1 s.

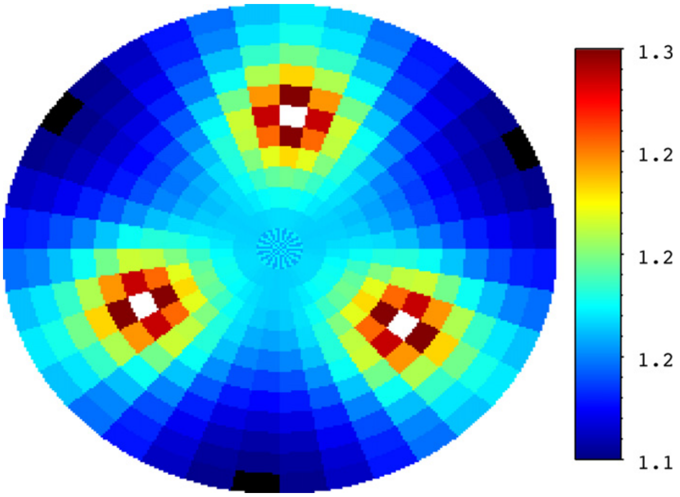

Fig. 6. Concentration distribution, 2d-model, 50 s.

We have constructed the simple model of hydride hydrogen tank with host alloy with high rates of sorption–desorption and have shown that this model produces reasonable results and describes main processes that take place in hydride tanks of different shapes and with different cooler configurations. The model is rather simple and can be used for engineering calculations. Also it is easily adjustable to different shapes, configurations, alloys, discretizations, and experimental conditions, and can be efficiently calculated on multi-processor computers.

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References

[1] L. Schlapbach, A. Züttel, Nature 414 (2001) 353–358.
[2] S. Satyapal, et al., Catal. Today 120 (2007) 246–256.
[3] M. Kandavel, V. Bhat, A. Rougier, L. Aymard, G.-A. Nazri, J.-M. Tarascon, Int. J. Hydrogen Energy 33 (2008) 3754–3761.
[4] P. Muthukumar, S.V. Ramana, J. Alloys Compd. 472 (1–2) (2009) 466–472.
[5] M. Botzung, et al., Int. J. Hydrogen Energy 33 (2008) 98–104.