EVALUATION OF KINETIC PARAMETERS OF HYDRIDE FORMATION

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Introduction

Metal-hydride technologies have excellent prospects for hydrogen storage. Kinetics of hydrogen sorption by hydride forming metals is now intensively studied worldwide. Mathematical modeling is able to help understanding the processes and to evaluate the kinetic parameters.

Results of this work are illustrated by uranium hydride as an example. We worked with the experimental data kindly presented by prof. J. Bloch, Israel [1]. They were curves of hydrogen sorption by uranium powder at consequent cycles of hydriding. The constant pressure was near equilibrium. This allowed keeping the temperature constant (370K). The pressure drop as a function of time was registered.

The sorption of hydrogen by uranium powder is conditioned by simultaneous reactions of absorption, desorption, diffusion through the hydride skin towards the phase bound, and formation of hydride phase (bound movement).

Thus the model appears as a boundary-value problem for the diffusion equation with moving bound with the Stefan-type condition on it and nonlinear boundary condition on the surface. This model together with the results of fitting the experimental data by the model curves and evaluations of the kinetic parameters are presented.

General assumptions

Particles of uranium have different sizes and forms. We chose two basic shapes to approximate the real particles: sphere and cylinder. In case of cylinders we consider them to be thin and long so that the influence of the butts can be neglected.

The density of uranium (18.9g/cm^3) is nearly twice more than the density of UH_3 (10.9g/cm^3). Sizes of the particles reduce from one cycle to another but we suppose that during the cycle the sizes remain unchanged.

In the experiment the pressure drop is registered. In [1] it is assumed that this is the same with the reaction fraction. We assume that it is the same with the relative amount of absorbed hydrogen. Obviously some hydrogen can dissolve in UH_3 and diffuse there. Equilibrium concentration in U is very low compared to UH_3 so we consider it to be zero. Diffusivity in UH_3 is much less than in U. Thus we consider the diffusivity in U to be very quick: all hydrogen dissolved in U is instantly delivered to the phase bound and spent on hydride formation. So the concentration on this bound is constant stoichiometric. The conservation law on the bound is an additional condition of the Stefan type.

On the surface of the particle there is the flux balance: absorption minus desorption is equal to diffusion. As desorption is square with respect to concentration near the surface, we have the nonlinear Neumann boundary condition.

We suppose spherical or cylindrical symmetry, i.e. concentration depends only on one spatial co-ordinate: radius in the appropriate curvilinear system. Under this assumption the diffusion equation becomes one-dimensional.

The model

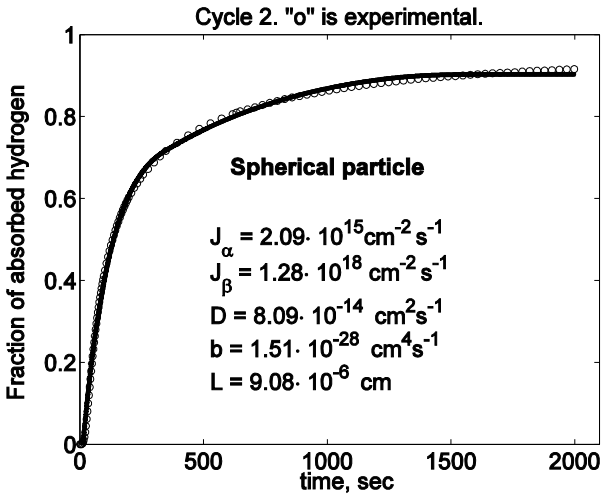
The process of hydriding of an uranium particle consists of three stages:

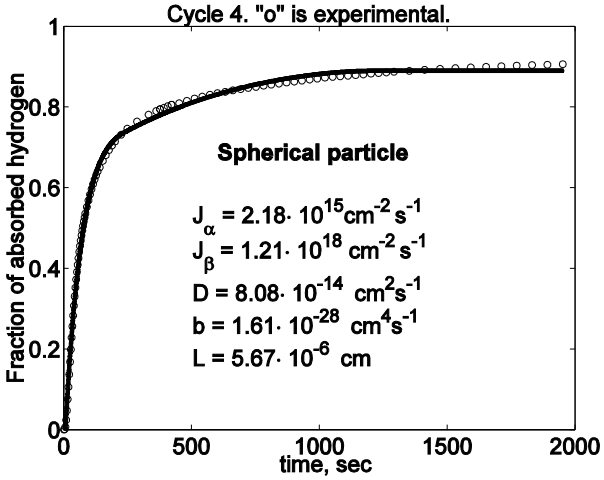
1. Skin development. Hydrogen is sorbed by both U and UH_3 surfaces and the nuclei of the new phase appear and grow till all the surface of the particle is covered by hydride. We model the nuclei to be symmetrical. Then the amount of the adsorbed hydrogen as a function of time can be obtained explicitly. It is a solution to the simple ordinary differential equation.
2. Skin growth (contracting envelope). Hydrogen is sorbed by the hydride surface, diffuses (rather slowly) to the phase bound and is spent on new hydride formation, making the skin wider. We model the process by the mentioned boundary-value problem for the one-dimensional diffusion equation in spherical or cylindrical co-ordinate system.
3. Final saturation. As soon as the uranium core disappears, i.e. the skin grows till the centre, the concentration in hydride grows towards the equilibrium level.

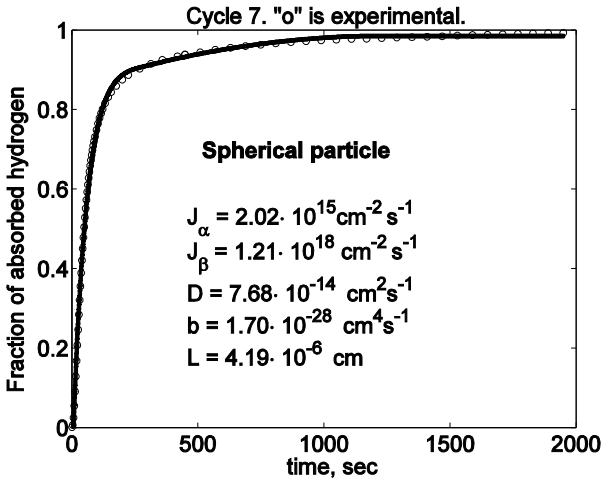
Results and discussion

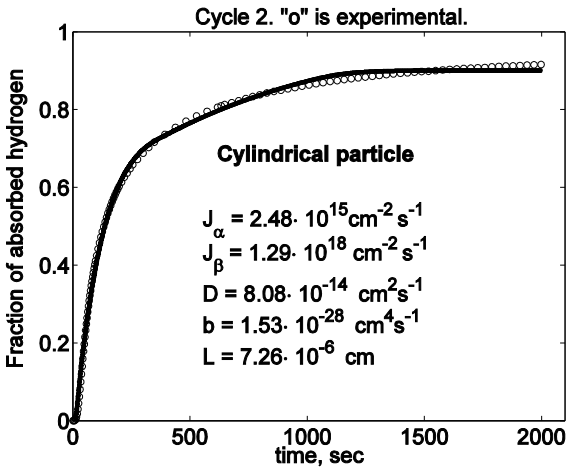
Here we present some approximations of the experimental curves by the model ones. Parameters are given in the figures.

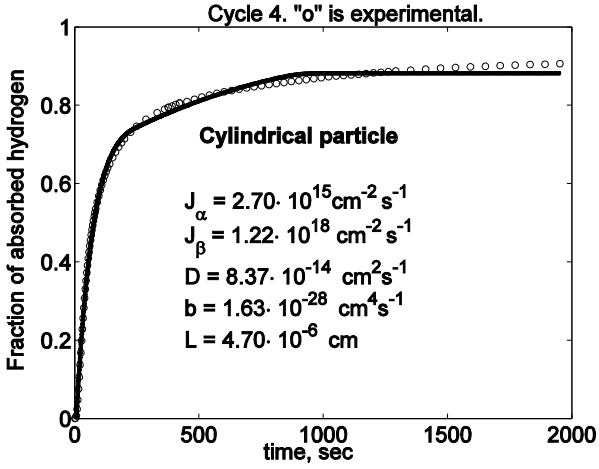
D: diffusivity in UH_3; b: desorption from UH_3; J_α: sorption density by U; J_β: absorption density by UH_3; L – radius of the particle.

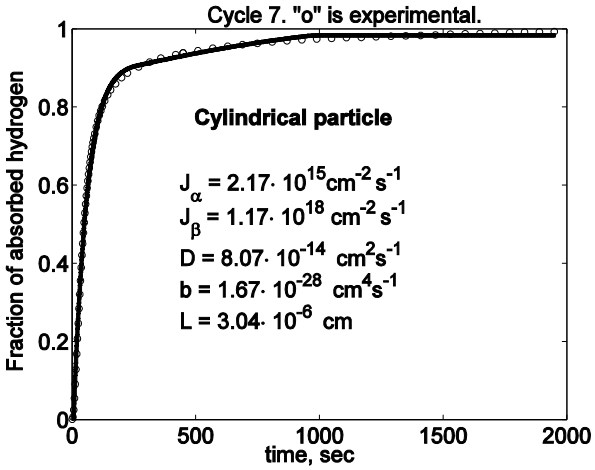












Conclusions

One can see that the coincidence is quite good, while the parameters change only a little; thus we can hope that these estimations are reliable.

We are grateful to prof. J. Bloch for the data.

References

1. Bloch J. The hydriding kinetics of activated uranium powder under low (near equilibrium) hydrogen pressure. Journal of Alloys and Compounds 2003;361:130–137.