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E.A. Denisov, M.V. Kompaniets, T.N. Kompaniets, V.I. Spitsyn

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Surface-limited permeation regime in the study of hydrogen interactions with metals

E.A. Denisov, M.V. Kompaniets, T.N. Kompaniets, V.I. Spitsyn
Saint-Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034, Russia
t.kompaniets@spbu.ru

Abstract
The application of permeation technique in the surface-limited regime for determining the rates of hydrogen absorption and desorption and terminal solid solubility for precipitation in hydride-forming metals is discussed in detail. The validity of various approximate expressions used to process the experimental data is verified by comparison with the results of computer simulation. Examples of the processing of the experimental curves obtained in the study of hydrogen permeation are presented, and the main attention is paid to possible limitations of the approximations used.

Keywords: Permeation; Surface-limited regime; Absorption and desorption rates; Terminal solid solubility

1. Introduction

Parameters of hydrogen interactions with metals are of a great interest for many branches of science and industry. Hydrogen isotopes are used (or inevitably present) in many present-day devices (for example gas or oil pipelines [1], nuclear reactors or steam generators [2, 3], containers for hydrogen isotope storage [4], etc.). Interacting with the metals surrounding the hydrogen-containing media, hydrogen permeates into the bulk of the wall material. The accumulation of hydrogen inside the metal results in a rapid decrease of the service lifetime of parts and components due to the hydrogen embrittlement [5, 6].

For hydride-forming metals and their alloys, which are used as structural materials (Ti, Zr), the main problem is delayed hydride cracking [7, 8]. At the first stages of hydrogen interaction with hydride-forming metals, a solid solution is formed. When the hydrogen concentration in the solution exceeds the so-called terminal solid solubility for precipitation (TSSp), all the additionally absorbed hydrogen is spent on hydride formation and does not take part in the permeation process. TSSp in Ti, Zr and their alloys in the α-phase is very low (several atomic percent) [9, 10]. The formation of hydrides leads to a degradation of the mechanical properties of the components due to hydrogen embrittlement and delayed hydride cracking [11-13]. For this reason, the data of hydrogen TSSp is of great importance for the selection of operation conditions and for the evaluation of the service lifetime.

The rates of the surface processes are of interest in many practical applications of hydrogen permeation. The process of hydrogen purification requires materials with a high rate of hydrogen permeation. In many cases, the rate of permeation through the metals and alloys with a high diffusion coefficient decreases as a result of the decrease in the rate of hydrogen dissociation due to the presence of admixtures in the hydrogen to be purified [14]. On the other hand, one of the ways to minimize leakage of hydrogen isotopes from fuel cells and hydrogen storage containers, which is especially important when using tritium, is a decrease in the dissociation rate of hydrogen and, consequently, the rate of adsorption on the surface [15].

The examination of various possible variants of hydrogen permeation through metals started more than sixty years ago in the paper [16], which gave a qualitative explanation of some peculiarities in permeation tests. Further development of the proposed approach [17-20]