

SOLID STATE PHYSICS

HYDROGEN-INDUCED NONEQUILIBRIUM OSCILLATING PHASE TRANSITIONS IN SOLID-STATE OPEN Pd-Sm-H SYSTEMS AND BELOUSOV-ZHABOTINSKII WAVES

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New phenomena in nonequilibrium open Pd-Sm-H systems have been observed: as a result of saturation with hydrogen followed by degassing, a one-phase system transforms into a two-phase one, and the two-phase system, into the one-phase one. This indicates the occurrence of nonequilibrium oscillating phase transitions. According to the hypothesis suggested by the authors, the observed phenomena are explained by competition between ascending and gradient diffusion under substantially nonequilibrium conditions of the open solid-state system.

Periodic chemical reactions, which have been known for a long time [1], have become the object of systematic studies after the discovery by Belousov [2] of an oscillatory chemical reaction in a homogeneous solution (oxidation of citric acid by potassium bichromate catalyzed by the Ce^{4+} - Ce^{3+} -ion pair) and subsequent Zhabotinskii's works [3]. Diverse variants of the Belousov-Zhabotinskii reaction were described. For instance, in an effectively stirred medium in a closed volume, the oscillations of the concentration of Br^- ions and the concentration ratio between Ce^{4+} and Ce^{3+} with a period of about one minute were observed for an hour as periodic changes in the solution coloration. If the necessary chemical substances were fed into the system (or removed from it), the ion concentration oscillations observed (the system color changes) may become continuous. In the absence of stirring, spatial inhomogeneities were formed in the system, and regular space-time pictures in the form of propagating wave fronts could be observed.

An analysis of periodic chemical reactions generalized in works on synergism and self-organization processes [4-7] shows that the most important reasons for their occurrence are the initial (and, probably, existing throughout the whole time of observations) deviations from equilibrium and the presence of at least several factors responsible for diffusive or other transformations of substances. From this point of view, it would be unjustified to rule out the possibility of oscillatory structural changes in solids, although observing such phenomena in solids is much more difficult than in liquids. Oscillatory changes are most probable in strongly perturbed solids, for instance, plastically deformed, irradiated, etc., especially in open systems such as metal-hydrogen. Earlier, we have reported data on oscillatory changes of the defective structure in the Pd-W-H system [8-11] and a superconducting ceramics [11, 12]. In this work, we describe nonequilibrium phase transitions of an oscillatory character in the Pd-Sm-H system.

METHODS AND EXPERIMENTAL RESULTS

Studies were performed for a Pd-8.2 at.% Sm alloy, the experimental procedure was described in [8, 9], and preliminary data were reported in [13]. Consider the results most characteristic in the context of this work. The (311) diffraction maximum of the FCC phase in the initial state (1), after three-stage

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saturation with hydrogen (2), and subsequent degassing (3) is shown in Fig. 1. At the initial state, the diffraction maximum had a Lorentzian shape indicating that the sample was single-phase. After saturating the sample with hydrogen for three times (saturation for 15 min at a 40 mA/cm² current density followed by degassing for 6 h, then saturation for 60 min at the same current density and degassing for 48 h, and, lastly, saturation for 60 min at a 80 mA/cm² current density), the diffraction maximum shifted to the lower values of the diffraction angle 2θ . This was indicative of the formation of the α -phase (interstitial Pd-Sm-H solid solution). After storing the sample for 27 000 h in air under normal conditions, the diffraction maximum returned approximately to the initial position, but its shape clearly indicated that the system had become two-phase and was comprised of Pd-Sm phases of different compositions. The maximum was resolved into two components, which made it possible to estimate the concentration of samarium in each phase. In the samarium-rich phase, the concentration was close to 10 at.%, and in the phase depleted of samarium, it was 7.5 at.%.

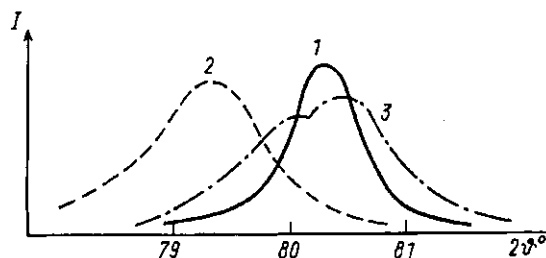


Fig. 1

The sample, which became two-phase, was again saturated with hydrogen for 120 min at a 80 mA/cm² current density. Measurements were taken 40 min after the saturation. They showed that the sample represented a Pd-Sm-H solid solution with high hydrogen content (Fig. 2, curve 2). The diffraction maximum was slightly asymmetric indicating the presence of traces of the Pd-Sm phase. Six hours after the saturation, the percentage of the Pd-Sm-H solid solution decreased approximately twofold, and in 400 h, the diffraction maximum returned to the position preceding the saturation with hydrogen (Fig. 2, curve 3). A comparison of the diffraction maxima measured prior to (curve 1) and after the last saturation allows us to state that sample relaxation during 400 h after the last saturation returned it into the single-phase state.

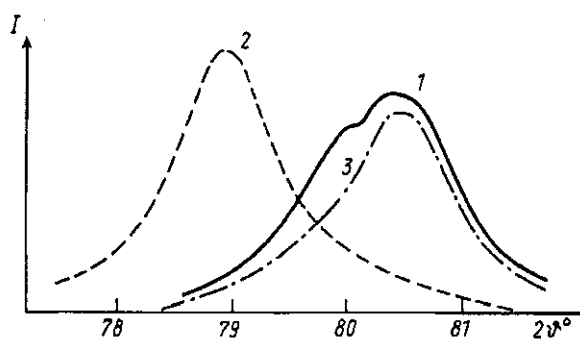


Fig. 2

To summarize, saturation with hydrogen of a Pd-8.2 at.% Sm single-phase sample and its degassing for 27 000 h caused the decomposition of the solid solution into two phases with samarium concentrations differing by 2.5 at.%. A more prolonged saturation of the resulting two-phase sample with hydrogen brought it into the single-phase state after degassing for 400 h. Clearly, the initial state and at least one of the final states were not equilibrium. It follows that the time dependence of the phase composition of the Pd-Sm-H system has an oscillatory character. This means that in nonequilibrium Pd-M-H systems, not only the

defective structure, as was shown in our works [8–12], but also the phase transitions proper can be of an oscillatory character.

DISCUSSION

Clearly, a rigorous theory of the observed phenomena with regard to an obviously nonequilibrium character of the system cannot be constructed at present. Nevertheless even now, the following hypothesis can be advanced. According to the equilibrium phase diagram [14], a Pd–Sm alloy containing 8.2 at.% of samarium should be two-phase at room temperature. Its single-phase character observed can be explained by very low rates of diffusion processes under usual conditions; diffusion slowness hinders attaining equilibrium by the system. The initial treatments with hydrogen caused not only a sharp increase in deviations from equilibrium but also acceleration of diffusion. As a result, in 27 000 h of degassing, the alloy approached equilibrium and therefore turned to be two-phase. Subsequent saturation with hydrogen (more energetic than all preceding ones) brought the sample into a state more distant from the equilibrium curve, and, on its return to the α phase during degassing, the sample arrived at a nonequilibrium single-phase state. From this standpoint, the observed phenomenon can be related to nonequilibrium phase transitions that occur far from equilibrium in the Pd–Sm–H system under incomplete relaxation conditions. Depending on the extent to which the initial and the final state deviate from equilibrium, the system can become either single- or two-phase. The greater the deviations, the higher is the probability that a single phase will be formed in $\beta \rightarrow \alpha$ transformations. It is easy to see that this reasoning is based on correlating the experimental data with the bifurcation diagrams [4–7]. Combining the perturbing action of saturation with hydrogen with subsequent relaxation in a certain way, we can induce oscillatory structural changes to a degree similar to Belousov–Zhabotinskii waves.

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