

PHYSICAL FACTORS OF THE $\alpha \rightarrow \beta$ TRANSFORMATION KINETICS IN A PALLADIUM-HYDROGEN SYSTEM

G. P. Revkevich, A. I. Olemskoi, M. A. Knyazeva, and A. A. Katsnel'son

X-ray diffraction methods were used to study the kinetics of the $\alpha \rightarrow \beta$ transformation in Pd exposed to electrochemical saturation with hydrogen. It was established experimentally that the kinetics of the $\alpha \rightarrow \beta$ transformation in the Pd-H system is described by the Avrami-type equation containing time to the first power. The observed time dependence of the saturation is related to the fairly high rate of growth of β -phase nuclei in a bounded volume. The incubation period t_0 and the logarithmic rate γ of growth of the β phase fraction were found to depend on the crystallographic orientation of the regions with respect to the flux of H atoms.

INTRODUCTION

Studying $\alpha \leftrightarrow \beta$ transformations in the Pd-H system has begun fairly recently [1-4]. Investigation of electrochemically hydrogenated specimens made it possible to suggest the mechanism of β -phase nucleation [1], to establish the time and orientation dependences of the β -phase fraction in the $\beta \rightarrow \alpha$ transformation [2], and to reveal the factors responsible for the β -phase stabilization [3, 4]. However, many specific features of the kinetics of β -phase nucleation have not been investigated so far.

The objective of this paper was to determine the law that describes the kinetics of the $\alpha \rightarrow \beta$ transformation and to find out how the ambient conditions affect the parameters of the kinetic equation.

SPECIMENS AND EXPERIMENTAL METHODS

The Pd specimens (stripes 0.1 mm thick) were hydrogenated at room temperature for various periods of time at a current density 2.5 mA cm^{-2} . The intensity of the X-ray diffraction maxima was measured by a DRON-UM1 X-ray diffractometer with the monochromatic Cu- K_α radiation and automatically recorded on the strip of an Endim-621.021 recorder. In the specific exposure conditions used, only those coherent scattering regions (CSR) participated in the formation of a particular diffraction maximum (hkl) in which the corresponding planes were parallel to the external surface of the specimen. For brevity sake we shall term these regions (CSR) (hkl). The measured intensity values were normalized to those calculated theoretically to obtain values proportional to the volume involved in the formation of the diffraction maximum (hkl). The content of the β -phase $p(t)$ in regions of different crystallographic orientation was calculated by comparing the normalized intensities of the diffraction maxima of the α - and β -phases with identical hkl . When calculating $p(t)$ it was taken into account that the line intensities corresponding to small diffraction angles may be weakened due to extinction and those corresponding to large diffraction angles, due to the presence in the specimen of defects of the first-class: point defects, their complexes, and small-radius dislocation loops. The methods used enable one to record β -phase contents exceeding 0.5%.

The sizes D of the coherent scattering regions and the microstrains ϵ were calculated by analyzing the widths of the diffraction maxima by the approximation method. The physical broadening β was found by the formula

$$B = \frac{(b + \beta)^3}{(b + \beta)^2 + \beta b} \quad (1)$$

Here b is the integral width of the reference specimen and B is the integral width of the specimen. The D and ϵ found in this way characterize the size of the coherent scattering regions and the microstrains normal to the specimen surface they contain.

EXPERIMENTAL RESULTS

The experimental data have shown that with saturation times of 7 and 10 min the β -phase lines do not manifest themselves, i. e., the fraction of the β -phase is less than 0.5%. As the time t increases, the fraction of the β -phase grows. The rate of growth of the β -phase volume fraction is maximum for CSR (100) and decreases in going over to CSR (311) and CSR (110) (Fig. 1).

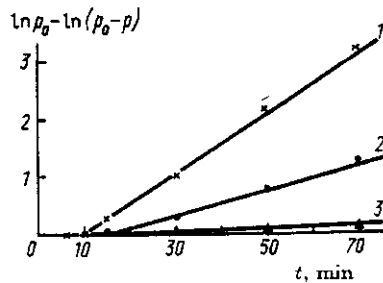


Fig. 1

Content of the β -phase as a function of saturation time in the CSR orientations: (100) (1); (311) (2); (110) (3) (p_0 is the final content of the β -phase).

The experimental values of $p(t)$ plotted using the logarithmic scale along one of the axes fit well the straight lines that do not pass through the origin. This means that for CSRs of each of the orientations the variation of the volume fraction of the β -phase can be described by the Debye relation

$$p(t) = p_0[1 - \exp\{-\gamma(t - t_0)\}]. \quad (2)$$

Here p_0 is the final content of the β -phase, γ is the logarithmic growth rate, and t_0 is the duration of the incubation period. The values of γ and t_0 calculated by the least squares method are given in Table 1. One can see that the orientation dependence for γ is more clear than for t_0 . The γ^{-1} values are related as 1 : 2.3 : 20 and the t_0 values as 1 : 1.5 : 1.7.

Table 1

Orientation of regions	$t_0 \times 10^{-2}, s$	$\gamma \times 10^4, s^{-1}$
(100)	6 ± 0.3	8.7 ± 0.3
(311)	9 ± 0.9	3.8 ± 0.2
(110)	10 ± 2.5	0.43 ± 0.06

DISCUSSION

1. Kinetic Equation

Empirical dependence (2) obtained for the $\alpha \rightarrow \beta$ transformation complies with the Avrami equation in the form

$$p(t) = p_0[1 - \exp\{-V_\beta n(t - t_0)\}], \quad (3)$$

where n is the nucleation rate in a unit volume and V_β is the volume of a precipitated particle of the β -phase. It has been shown earlier [1] that upon electrochemical saturation the β -phase nuclei have the shape of plates whose normals coincide with the direction of the flux of hydrogen atoms. In this connection the time dependence of the volume $V_\beta = SD$ (\mathcal{D} is the plate thickness and S the cross section) is determined by the time dependence of the plate thickness \mathcal{D} . It should be noted that the CSR size found from analyzing the diffraction maxima coincides with the plate thickness. The present paper has experimentally demonstrated that the plate thickness $\mathcal{D} = 15 \times 10^{-6}$ cm remains unchanged with increasing saturation time and equals the CSR thickness of the initial α -phase.

The time Δt of growth of the plate with the thickness \mathcal{D} can be assumed equal to $\Delta t \approx \mathcal{D}^2/2D \approx 4 \times 10^{-4}$ s (the diffusion coefficient is $D \approx 3 \times 10^{-7}$ cm² s⁻¹ [5]), i. e., it is considerably smaller than the characteristic saturation time $t \geq 10^2$ s. Hence, the constant values of \mathcal{D} and V_β stem from the fact that the β -phase regions grow in the bounded volume of the α -phase CSR. Our estimates have shown that the conditions $t \gg \Delta t$ and $V_\beta = \text{const}$ for polycrystalline specimens are always valid if the saturation time is more than a few seconds.

In this case the γ coefficient in (2) depends only on the rate of nucleation n . As a whole the kinetics of the $\alpha \rightarrow \beta$ transformation is determined by t_0 and n . Let us consider how the experimental conditions affect the above parameters.

2. Incubation Period

Supercooling as a necessary condition for nucleation of the β -phase. We make use of the concepts of the kinetic theory of first-order phase transformations. In accordance with the fluctuation theory, the incubation period for the origination of a nucleus of a critical size R_c is

$$t_0 \approx \frac{R_c}{v} \exp \left\{ \frac{\Delta \mathcal{F}(R_c)}{T} \right\}, \quad (4)$$

where T is the temperature, $\Delta \mathcal{F}(R_c)$ is the variation of free energy due to the formation of a nucleus with the radius R_c , and v is the velocity of the boundary movement. In terms of microscopic approximation, the surface energy is determined by the coefficient of surface tension, σ , and the bulk energy, by the variation of the energy density due to phase transformation

$$g(T) = (1 - T/T_0)q - (E_{el} + E_d). \quad (5)$$

Here T_0 and q are, respectively, the temperature and the specific heat of phase transformation, E_{el} and E_d are the elastic energy of nucleation per unit volume and the energy of defect structure. The effect of σ on the incubation period t_0 will be discussed below. Substituting the expression for the critical radius $R_c = \sigma/g$ into (4), we ultimately arrive at the expression for the incubation period

$$t_0 \approx \frac{\sigma}{gv} \exp \left\{ a \frac{\sigma^3}{g^2 T} \right\}, \quad (6)$$

where $a \approx 1-10$ is a constant depending on the nucleus shape. A necessary condition for nucleation of a new phase is the condition $g > 0$, which can only be ensured by strong supercooling

$$T - T_0 > \frac{E_{el} + E_d}{q} T_0. \quad (7)$$

At the given q , E_{el} , and E_d , this can be achieved by either lowering the experimental temperature T or increasing the temperature of phase transformation T_0 .

From the Pd-H phase diagram [6] it is known that the critical temperature of transformation is $T_c = 571$ K and the appropriate pressure $P_c = 19.87$ atm. Since the saturation occurs at room temperature, the limit supercooling $T_c - T \approx 280$ K can be attained by a pressure growth up to P_c . In electrochemical saturation, the pressure and current density are related by the expression $P = 1.7 \times 10^4 j$ A cm⁻² [7]. Then P_c is attained by means of a current density $j_c = 1.17$ mA cm⁻². In our experiment $j = 2.5$ mA cm⁻²,

from which it follows that $j > j_c$, so the system is in a single-phase region. In this case condition (7) for convenience is written as

$$\Delta T(j) > \frac{E_{el} + E_d}{q} T_0, \quad (8)$$

where $\Delta T(j)$ is the effective supercooling ensured by a given density of saturation current.

A substantial growth of j with respect to j_c increases the supercooling $\Delta T(j)$ so much that the incubation period (6) practically takes on the zero value. The experiment conducted with the current density $j = 25 \text{ mA cm}^{-2}$ has shown that the incubation period is practically absent.

The effect of the elastic energy. The elastic energy $E = E_{el}\Omega$ per atom with a volume Ω in a continuous approximation takes the form [8]

$$E = \frac{1}{2} \mathcal{A}(\mathbf{n}) \delta^2. \quad (9)$$

Here $\mathcal{A}(\mathbf{n})$ is the effective modulus of elasticity multiplied by the atomic volume, $\delta = 0.03$ is the lattice strain in the $\alpha \leftrightarrow \beta$ transformation. Given this δ value, the nuclei take the shape of plates. Calculation by (9) for the given elastic constants $C_{11} = 2.2378 \times 10^{12} \text{ dyne cm}^{-2}$, $C_{12} = 1.7312 \times 10^{12} \text{ dyne cm}^{-2}$, $C_{44} = 0.7125 \times 10^{12} \text{ dyne cm}^{-2}$ [9] and the lattice parameters $a_\alpha = 3.894 \text{ \AA}$ and $a_\beta = 4.027 \text{ \AA}$ for the α - and β -phases, respectively, [6] yields $E(100) = 183 \text{ K}$, $E(311) = 236 \text{ K}$, $E(110) = 313 \text{ K}$, and $E(111) = 346 \text{ K}$ for $E(hkl)$ of different orientations. Thus, the elastic energy of generation of a plane equilibrium nucleus will depend considerably on the crystallographic orientation of the nuclei.

It is this dependence that is responsible for different incubation periods of nuclei of different orientations. The values of t_0 are related as 1 : 1.2 : 1.6 : 1.8 for the above $E(hkl)$ for the (100) (311), (110), and (111) CSRs, which is consistent with the experimental data presented above.

The effect of surface tension. According to (6) the incubation period is determined not only by the variation of the free energy g but also by the coefficient of surface tension σ . Therefore, the dependence of t_0 on hkl can also be related to the orientation dependence $\sigma(hkl)$. Thus, for a f.c.c. crystal-liquid interface the coefficient of surface tension rises in the sequence (111), (100), and (311). At the same time t_0 is observed to rise in a different sequence. Two factors can account for this. First, in passing from the crystal-liquid interface to the interphase boundary the succession of orientations leading to a growth of σ can vary. Second, the variation in σ for different orientations may turn out to be less important than the corresponding variation in the elastic energy.

The effect of defect structure. The defect structure can play an important role in the kinetics of the $\alpha \rightarrow \beta$ transformation. In order to clarify this point, we carried out the following experiment. A stripe presaturated with hydrogen for 30 min at a current density 2.5 mA cm^{-2} was then degassed in air for 1600 h. When the stripe was subsequently saturated under the same regime, not even traces of the β -phase were observed. We could obtain the β -phase for the second time only after the density of the saturation current was increased up to 3.75 mA cm^{-2} . This can be explained in the following way.

Initially, before the first saturation, the specimen was characterized by the microstrain $\varepsilon = 1.5 \times 10^{-3}$ in the CSR (100), which corresponds to the density of randomly distributed dislocations $\rho = 1.2 \times 10^{10} \text{ cm}^{-2}$ [10]. Prior to the second saturation the dislocation density grew up to $4.8 \times 10^{10} \text{ cm}^{-2}$. This means that before the second saturation $E_d \propto \rho$ was four times that before the first saturation, which violates the condition of the β -phase nucleation (8). In order to meet condition (8) it is necessary to raise the density of the saturation current to thereby increase $\Delta T(j)$. Then E_{el} undergoes a change of no more than 1%.

3. The Rate of Nucleation of the β -Phase

The fluctuation theory determines the rate of nucleation n as [8]

$$n \propto \exp\left\{-\frac{a\sigma^3}{g^2T}\right\} \exp\{-U/T\}. \quad (10)$$

This expression is distinguished from (6) by a factor depending on the energy of migration of the interphase boundary U along its potential relief. The influence of the supercooling $\Delta T(j)$, of the elastic self-energy E_{el} , and of the energy of defects E_d on n^{-1} and, hence, on γ^{-1} turns out to be largely the same as on the

incubation period t_0 (for discussion see above). Therefore, we analyze the influence on π of the second factor alone.

In contrast to the energy of elastic distortions, which is proportional to the square of the strain that arises in the $\alpha \rightarrow \beta$ transformation due to the difference in the specific volumes of the α - and β -phases, the energy of interaction between the boundary and the field of elastic stresses varies linearly (one has to take into account the strain produced by the defect structure, too)

$$U = U_0 + B(\delta + \varepsilon). \quad (11)$$

Here the energy of migration of the interphase boundary in an ideal crystal U_0 and the parameter of interaction of the boundary and the elastic field B are determined by the orientation of CSR. Since the strains δ and ε are 10^{-2} and 10^{-3} , respectively, comparison of equalities (9) and (11) demonstrates that the migration energy (11) must show a stronger orientation dependence as compared to the variation of the thermodynamic potential (5). This implies that when the CSR orientation changes, the corresponding change of the increment γ must be greater than the change of the incubation period. Indeed, as was pointed out above, for the (100), (311), (110) sequence of orientations we have the 1 : 1.5 : 1.7 ratio for t_0 , whereas for γ^{-1} the ratio is 1 : 2.3 : 20. According to (6), (10) these ratios hold if $U(311) - U(100) \approx 128$ K and $U(110) - U(100) \approx 758$ K. Such a marked difference in the $U(hkl)$ values corroborates the validity of linear dependence (11). On the other hand, it means that the orientation dependence of the $\gamma(hkl)$ parameter must not vanish even with a considerable increase of the current density. This dependence is indeed observed in experiment even at $j = 60$ mA cm $^{-2}$.

CONCLUSION

It has been experimentally established that the kinetics of the $\alpha \rightarrow \beta$ transformation in the Pd-H system can be described by the Avrami equation containing time t to the first power

$$p(t) = p_0[1 - \exp\{-\gamma(t - t_0)\}], \quad \gamma = V_\beta n.$$

The incubation period t_0 depends on the crystallographic orientation of regions, in which the β -phase is nucleated, with respect to the flux of hydrogen atoms, on the saturation current density, and on the presence of defects in the specimen. A stronger orientation dependence of the logarithmic rate of growth γ of the volume fraction of the β -phase in comparison to t_0 has been detected.

The study carried out has shown that the orientation dependence of the elastic energy of the β -phase nucleation is a determining factor in the dependence of t_0 on the CSR crystallographic orientation. An increase of the degree of supercooling $\Delta T(j)$, which depends on the saturation current density j , brings about a decrease of t_0 . An enhanced number of defects (i. e., growth of E_d) in the initial state leads to a longer incubation period.

Variation in the volume fraction of the β -phase in time has been found to depend on the rate of nucleation n alone since it is high ($V_\beta = \text{const}$).

The finding that n depends on the CSR orientation stronger than t_0 is associated with the strong orientation dependence of the migration energy of the interphase boundary, $U(hkl)$.

REFERENCES

1. G. P. Revkevich, S. V. Sveshnikov, A. A. Katsnel'son, and V. Khristov, *Izv. Vuzov. Fizika*, vol. 31, no. 6, p. 117, 1988.
2. G. P. Revkevich, A. A. Katsnel'son, and V. Khristov, *Vest. Mosk. Univ. Fiz. Astron.*, vol. 29, no. 3, p. 72, 1988.
3. G. P. Revkevich, S. V. Sveshnikov, and A. A. Katsnel'son, *Izv. Vuzov. Fizika*, vol. 31, no. 5, p. 102, 1988.
4. G. P. Revkevich, A. A. Katsnel'son, and V. Khristov, *Metallofizika*, vol. 11, no. 3, p. 57, 1989.
5. S. D. Axelrod and A. C. Makrides, *J. Phys. Chem.*, vol. 43, no. 1, p. 50, 1969.
6. Yu. V. Levinskii, *Constitution Diagrams* (in Russian), Moscow, 1975.

7. G. Borelius and S. Lindblom, *Ann. Phys.*, vol. 82, p. 201, 1927.
8. A. A. Katsnel'son and A. I. Olemskoi, *Microscopic Theory of Nonhomogeneous Structures*, Mir Publishers, Moscow, 1990.
9. D. K. Hsu and R. G. Leizure, *Phys. Rev.*, vol. B20, no. 4, p. 1339, 1979.
10. M. A. Krivoglaz, *The Theory of Scattering of X-Rays and Thermal-velocity Neutrons by Real Crystals* (in Russian), Moscow, 1967.

5 July 1991

Department of Solid State Physics