Journal of Engineering Physics and Thermophysics, Vol. 74, No. 5, 2001

PHASE STATES OF HYDROGEN IN METALLIC PALLADIUM

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UDC 541.183.1

The authors consider the experimental dependence of the integral interatomic binding energy in palladium on the relative atomic concentration of hydrogen that is absorbed in the palladium. It is shown that the hydrogen in the palladium exists in atomic, molecular, and chemically bonded form. Examples of using the results obtained in investigation of heterogeneous catalysis on transition d-metals are presented.

In 1961, the results of measurements of the dependence (see Fig. 1) of the integral interatomic binding energy E in palladium on the relative atomic concentration C of hydrogen absorbed in the palladium were published in [1–3]. These measurement results were obtained using a specially developed method [3–5]. The dependence of the paramagnetic susceptibility of palladium χ on C [6] is also illustrated in Fig. 1.

Analysis of the dependence of E on C shows that in the interval of C from 0 to 0.1 E decreases, on the average, almost linearly with increase in C. The energy ΔE, extracted from the gas of collective (valence) electrons of palladium, increases by approximately the same law:

$$\Delta E = 110 - E\,(C)\ ,$$

where 110 is the maximum value of the integral interatomic binding energy in the palladium and $E(C)$ is the running value of the binding energy.

In the interval of C under consideration, the numerical value of this energy (ε_λ) that accounts, on the average, for one hydrogen atom is

$$\varepsilon_\lambda \approx \frac{\Delta E}{\Delta C} \approx \frac{110 - 77}{0.1} \approx 330\ \text{kcal/mole} \tag{1}$$

(or ≈ 14.5 eV per Pd atom); this value coincides well with the ionization energy of the hydrogen atom (≈ 13.6 eV [7]). This allows an assumption that in the interval of C from 0 to 0.1 hydrogen in the palladium exists in the form of protons screened by electrons or in the form of so-called screened complexes $(H^+)_{sc}$, which corresponds to the data obtained earlier [8, 9]. In addition, the process of ionization of the hydrogen atom does not change energetically the state of the electron gas of the palladium, since the neutral hydrogen atom, soluble in it, adds a kinetic energy equal to 13.6 eV to the metal, which is very close to the value obtained from formula (1).

It is well known [10] that in absorption hydrogen in the crystal lattice of palladium is located mainly at octahedral interstices, whose number corresponds to that of the palladium atoms. This is accompanied by

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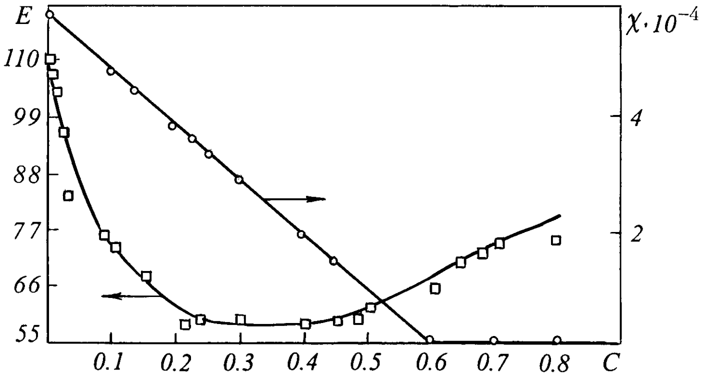

Fig. 1. Dependences of the sublimation energy (integral) E (kcal/mole) and the paramagnetic susceptibility χ (mole^{-1}) of the system Pd–H on the concentration of hydrogen C = H/Pd (atomic relation).

the filling of holes in the 4*d*-shells of the palladium atoms with electrons, whose mean number per palladium atom is equal to 0.36 [11, 12].

For comparison with this value, for the FCC crystal lattice of palladium we calculated the number of covalent-bonded pairs of palladium atoms from the number of atoms occurring at the centers of the adjacent lattice faces that accounts, on the average, for one palladium atom; this number turned out to be equal to 0.37.

This agreement of the indicated values suggests that the metallic palladium in the α-phase by 36–37% consists of the molecular complexes Pd_2^+ of covalent-bonded pairs of atoms in one of which a hole in the 4*d*-shell is localized.

It can also be assumed that the screened complexes $(H^+)_{sc}$, diffusing into the palladium, collide with the complexes Pd_2^+ and destroy them, for example, according to the equation

$$(H^+)_{sc} + Pd_2^+ \to PdH + Pd\ (+\,\varepsilon_{th})\,, \qquad (2)$$

which, basically, corresponds to the well-known fact of the formation of the β-phase of palladium, i.e., to a palladium hydride.

Thus, in the interval of C considered, the hydrogen in the palladium exists both in the form of screened complexes that are neutral hydrogen atoms in total charge and as part of the molecules of palladium hydride.

The assumption of the existence of the molecular complexes Pd_2^+ in the palladium allows us to draw an important, in our opinion, conclusion in the field of heterogeneous catalysis on palladium in particular and on transition *d*-metals as a whole.

The complex with a hole in the last *d*-shell possesses considerable free energy and, being located on the metal surface, can be the initiator of chemical reactions upon inelastic collision with it of adsorbate molecules from the gaseous phase in catalysis, i.e., can be an active center.

In our opinion, in the interval of C from 0.1 to 0.2 (see Fig. 1) the process of inelastic destruction of the molecular complexes Pd_2^+ according to Eq. (2) continues. From the free palladium atoms a second generation of the complexes Pd_2^+ is formed, which, just as the first ones, are destroyed. Similar complexes of the third, fourth, etc., generations are formed and destroyed, during which each subsequent generation of the complexes Pd_2^+ has a smaller value of the energy of covalent bonding forces than the previous generation.

The decay of the complexes Pd_2^+ in the interval of concentration of hydrogen from 0 to 0.2 is accompanied by a decrease in the energy of covalent bonding forces of the palladium atoms virtually to zero. Here the total energy of interatomic binding in the palladium decreases from 110 to 59 kcal/mole, which is explained by the very short time of settled life of the hydrogen in octapores ($\approx 10^{-9}$ sec [13]).

From the above data, at least for palladium, it is possible by means of the obtained dependence of E on C (see Fig. 1) to find new data on the structure and quantities that comprise the total energy of interatomic binding of atoms in the palladium:

$$E = E_{\text{cov}} + E_{\text{m}} = 51 \text{ kcal/mole} + 59 \text{ kcal/mole} = 110 \text{ kcal/mole} .$$

The following equality also holds:

$$\varepsilon = \varepsilon_{\text{cov}} + \varepsilon_{\text{m}} .$$

We obtained numerical values of ε, ε_{cov}, and ε_{m}:

$$\varepsilon \approx 4.8 \text{ eV}, \quad \varepsilon_{\text{cov}} \approx 3.1 \text{ eV}, \quad \varepsilon_{\text{m}} \approx 2.6 \text{ eV} .$$

The approximate equality of ε and $\varepsilon_{\text{cov}} + \varepsilon_{\text{m}}$ confirms the assumptions made.

Using the formula for determining the sum of terms of an infinitely decreasing geometric progression, it can be established that the process of formation and destruction of the molecular complexes Pd_2^+, in which the zero value of the number of holes in the 4*d*-shells of the palladium atoms can be attained, is completed for $C = 0.72$, which corresponds to the data obtained in investigation of the phenomenon of palladium superconductivity [14] and somewhat differs from the value of $C = 0.6$ (see Fig. 1) that is obtained in investigation of the paramagnetic susceptibility χ [6]. In our opinion, this is due to the insufficient sensitivity of the method for measuring this parameter, by which it is possible, apparently, to record only three generations of holes in the 4*d*-shells of the palladium atoms.

Thus, over the entire interval of C from 0 to 0.2 the hydrogen in the palladium exists in the form of screened complexes and as part of the molecules of palladium hydride.

In the interval of C from 0.2 to 0.5, as is indicated by the performed calculations of the limiting value of the concentration of hydrogen for which the process of filling the holes in the 4*d*-shells of the palladium atoms ceases, the process of formation of palladium hydride according to reaction (2) is still dominating. However, this process involves both the first and subsequent generations of the complexes Pd_2^+ having different progressively decreasing values of the energies of covalent bonding forces. In addition, the behavior of E as a function of C (see Fig. 1) in the given section shows that the occurring processes of formation of the subsequent generations of the complexes Pd_2^+ and of decay of the previous generations with account for the thermal effect of reaction (2), equal to 9.6 kcal/mole, are energy-balanced.

The integral energy of interatomic bonds in the palladium in the given interval of concentration of hydrogen is determined mainly by metallic bonding forces, which are equal to 59 kcal/mole or ≈2.6 eV per Pd atom.

As the behavior of E as a function of C (see Fig. 1) indicates, in the interval of C from 0.5 to 0.8, we observe a considerable growth in the integral interatomic binding energy E from 59 to 78 kcal/mole in the palladium. In this interval of C, the specific interatomic binding energy ε_λ in the palladium that accounts, on the average, for one hydrogen molecule is

$$\varepsilon_\lambda \approx \frac{\Delta E}{0.5 \Delta C} \approx \frac{78 - 59}{0.5 \cdot 0.3} \approx 125 \text{ kcal/mole} ,$$

or ≈5.5 eV per Pd atom.

The result obtained coincides rather well with the value of the energy of formation of a hydrogen molecule (4.77 eV per H atom [7]). This suggests that the process of formation of molecular hydrogen from atomic hydrogen, previously absorbed by the palladium, is dominating in the interval of C under consideration.

NOTATION

$\varepsilon_{\mathrm{th}}$, thermal effect of the reaction of formation of palladium hydride, kcal/mole; E_{cov}, component of covalent bonding forces, kcal/mole; E_{m}, component of metallic bonding forces, kcal/mole; ε, total interatomic bonding energy in palladium per Pd atom, eV; $\varepsilon_{\mathrm{cov}}$, energy of covalent bonding forces of an atom pair in the complex Pd_2^+ per Pd atom, eV; ε_{m}, energy of metallic bonding forces per Pd atom, eV. Subscripts: th, thermal; cov, covalent; m, metallic; sc, screened.

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