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## Valence state of hydrogen in hydrides of intermetallic compounds

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The experimental data on the mechanism of hydride dispersion of intermetallic compounds of the $LaNi_5$ type and the crystal structures of hydride phases based on these compounds were analyzed. A new approach was suggested and substantiated, which allows one to consider hydride dispersion as a result of a redox process associated with the formation of $H^{\delta-}$ hydride ions at concentrations of hydrogen in the solid hydride $C_H \geq C_{H_{cr}}$. The value of $C_{H_{cr}}$ is determined by the redox potential of the reaction $H^{\delta+} + M^{\delta-} \rightleftharpoons H^{\delta'-} + M^{\delta'+}$.

**Key words:** intermetallic compound, mechanism of hydride dispersion, redox process, hydride ion.

Previously, we have found that two forms of hydrogen dissolved in the $LaNi_5$ and $CeCo_5$ intermetallic compounds (IMC) coexist in the region of the plateau or in the region of the equilibrium in the IMC—hydrogen system, which is invariant at a constant temperature.[1] Later on, the generality of this phenomenon, at least for intermetallic compounds, which crystallize in the $CaCu_5$ structural type, was confirmed.[2—6] "Calorimetric titration," which was used for the first time in Ref. 1, appeared to be very informative and useful not only for studying equilibrium states in IMC—$H_2$ systems but also for studying the dynamics of the attainment of the equilibrium at various concentrations of hydrogen in the solid phase, including the mechanism of "hydride dispersion" or spontaneous (without mechanical treatment) conversion of a monolithic sample of the alloy into a virtually monodisperse powder, which absorbs up to 1000 volumes of $H_2$ per volume of the solid phase, upon its repeated cycling under an atmosphere of hydrogen.[7—9]

It is commonly supposed that at low concentrations of hydrogen in the solid phase, H atoms are randomly distributed over the 6m and 12n positions of the $CaCu_5$ structural type, and when the concentration reaches the critical (for a particular intermetallic compound) value $C_{H_{cr}}$, the solid solution becomes ordered, which is accompanied by a sharp stepwise increase in the volume of the solid phase.

Analysis of the experimental data[1—5] and the values of the volume effects associated with the formation of an "ordered" solid solution in IMC—$H_2$ systems or, to put it differently, of a hydrogen sublattice in the β hydride phase, allows one to tackle the problem of the valence state of hydrogen in Pd—$H_2$ systems, which has been the subject of discussion within the last five decades, in a new fashion. If the intermetallic compound contains a rare-earth element and crystallizes in the $CaCu_5$ structural type, Laves phases, or in similar structural types, the IMC—$H_2$ systems also belong to the above-mentioned systems. The discussion of this fundamental prob-

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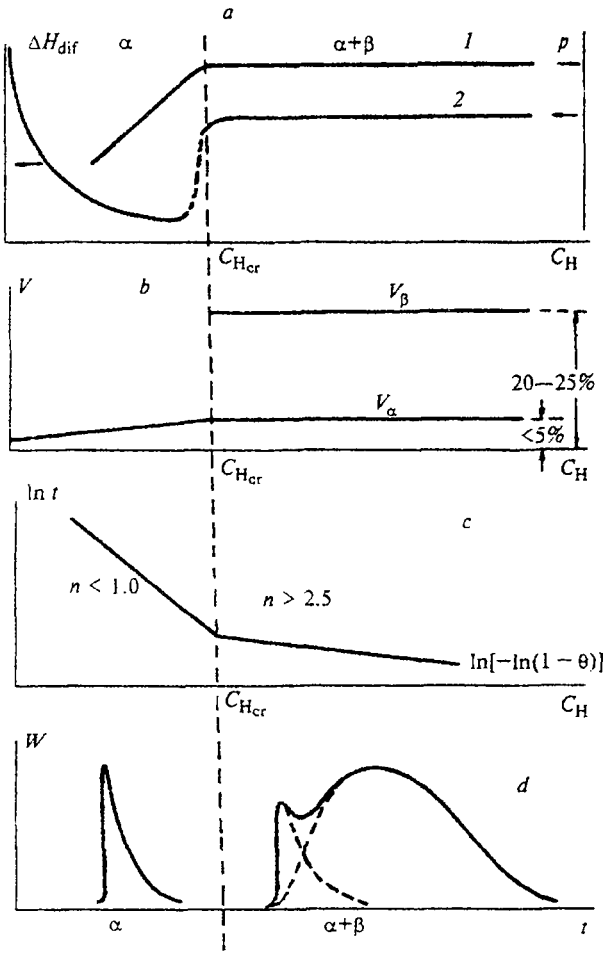


**Fig. 1.** Thermodynamic and kinetic characteristics of interactions in the IMC—$H_2$ system in the α (the region of the solid solution of hydrogen in the intermetallic compound) and α+β (the region of the solid solution and the β hydride phase) regions of the phase diagram:
*a*, the dependences of the equilibrium pressure ($p$) (curve *1*) and the partial molar enthalpy of dissolution of hydrogen ($\Delta H_{dif}$) (curve *2*) on the concentration of hydrogen ($C_H$) in the intermetallic compound at a constant temperature;
*b*, the change in the volume of the lattice ($V$) after formation of the α and β phases;
*c*, the change in the mechanism of hydrogenation of the intermetallic compound (the kinetic curves in logarithmic coordinates);
*d*, the profiles of the curves of heat evolution (heat absorption in the case of calorimetric titration of the intermetallic compound with hydrogen); $W$ is the thermal emission, and $t$ is the time.

lem in the chemistry of hydrides has been started in the classical work by Ubbelode,[10] who introduced the concept of the positively charged H atom, and in the work by Gibb,[11] who suggested a model with a negatively charged $H^-$ hydride ion.

In Fig. 1, which has a generalized character, the following dependences based on the data obtained in various experimental works (including Refs. 1—6) are compared: (1) the isotherms, which describe the equilibrium pressures of hydrogen in IMC—$H_2$ systems at different temperatures below critical (see Fig. 1, *a*); (2) the differential enthalpies of hydrogenation $\Delta H_{dif}$ or heats of hydrogenation $Q$ at constant temperature (Fig. 1, *a*); (3) the dependence of the volume of the solid phase on the amount of absorbed hydrogen or, to put it differently, the volume effects of the reaction of formation of a disordered solid solution of hydrogen (α phase) and ordered (in the crystalline phase) β hydride (see Fig. 1, *b*); (4) the results of experiments on the dynamics of the attainment of equilibrium states (so-called "kinetic curves") processed using Erofeev—Avrami's equation:

$$-\ln(1-\theta)]^{1/n} = kt$$

where $t$ is the time of the attainment of the equilibrium, θ is the degree of hydrogenation or, to put it differently, the hydrogen content of the solid phase ($C_H$), and $n$ is the parameter, whose value makes it possible to judge the mechanism of the reaction (see Fig. 1, *c*); (5) the profiles of the heat signals upon absorption of hydrogen in the α region and in the region of the plateau obtained by the Calvet calorimetric method (see Fig. 1, *d*).

Analysis of the data given in Fig. 1 demonstrated that in the systems under consideration there is a "special" point (or the critical value $C_{H_{cr}}$) at which both types of the equilibrium $p,T,C$ and $Q,T,C$ diagrams and *the mechanism of the chemical reaction* of hydrogen with metal, which proceeds with retention of the structural type of the initial intermetallic compound throughout the $C_H$ range, are radically changed. The change in the mechanism of the chemical reaction is particularly sharp, pronounced, and, what is more important, stepwise.

The change in the profile of the heat signal of a Calvet calorimeter, *i.e.*, in the time of the attainment of the equilibrium in the system, in going from the α region to the plateau (see Fig. 1, *d*) also indicates that the chemical reaction of absorption of hydrogen in the α region and in the region of the plateau occurs according to different mechanisms.

When the concentration of hydrogen in the solid phase reaches $C_{H_{cr}}$, the volume of the solid phase increases spontaneously (virtually at room temperature and at a pressure of $H_2$ of several atmospheres) by 10—15% and 12—25% for individual metals and intermetallic compounds, respectively. The anomalously large volume effect of this reaction, which is associated with the formation and growth of embryo of a new β hydride phase, is the cause of hydride dispersion or "embrittlement" of a compact metal sample or an intermetallic compound to form a disperse sample. In this case, we discuss only the cause of "embrittlement" of the solid phase when it is saturated with hydrogen rather than the mechanism of this process.

The change in the mechanism of absorption of hydrogen at the "special" point, namely, the change from the diffusion mechanism when $n < 1$ in the α region to

the mechanism of the "chemical reaction" to form a new chemical compound when $n > 2.5$ in the region of the plateau, is accompanied by a very large increase in the volume of the solid phase with retention of the structural type of the crystal lattice-matrix. Therefore, it would appear reasonable that the appearance of crystallization centers or embryos of a new β hydride phase is directly associated with the change in the effective volume of H atoms when the hydrogen sublattice becomes ordered in the region $C_H > C_{H_{cr}}$, which is, apparently, due to the change in the valence state of hydrogen at this point.

The change in the effective volume of H atoms in going from the α solid solution to the "chemical compound" (the β hydride phase) can be estimated based on the results of experimental studies of crystal structures of α and β phases in various IMC—$H_2$ systems, for example, in the $LaNi_5$—$H_2$ system.[12—15] According to these data, H atoms occupy the same tetrahedral or quasitetrahedral 6m and 12n sites with the effective radii of 0.25—0.30 Å (α phase) and 0.35—0.40 Å (β phase). The effective volumes of these tetrahedral cavities in the α phase and in the structure of the initial intermetallic compound are virtually identical. A rather small increase in the interatomic La—Ni and Ni—Ni distances to 3.11 and 2.69 Å, respectively, appears to be sufficient for a stepwise increase in the volume of the solid phase by 20—25% when $C_H \geq C_{H_{cr}}$.

A process involving a change in the valence state, namely, the *redox process* sensitive to the concentration of an oxidizing agent (for example, the process according to the mechanism $H^{\delta+} + M^{\delta-} \longrightarrow H^{\delta'-} + M^{\delta'+}$, where $H^{\delta'-}$ and $M^{\delta'+}$ are the metal matrices (the intermetallic compound) in the α and β phases, respectively) can be considered as the most probable process, which causes the sharp increase in the effective volume of H atoms when the concentration of the "saturated solid solution" is attained ($C_H \geq C_{H_{cr}}$). This suggestion is supported by a high lability of hydrogen atoms in α phases compared to β phases, which was reported in the literature many times, and a sharp (by several orders of magnitude) decrease in the conductivity in the M—$H_2$ systems at the moment of the appearance of the β hydride phase.

The approach under consideration makes it possible to construct a phenomenological model, which adequately describes the state of hydrogen dissolved in the intermetallic compound in different regions of the $p,T,C$ phase diagram as a result of the reverse reaction

$$H_2 + M \rightleftharpoons H^{\delta+} + M^{\delta-} \underset{\text{at } C_H > C_{H_{cr}}}{\rightleftharpoons} H^{\delta'-} + M^{\delta'+}$$

According to this model, hydrogen atoms, which are chemisorbed on active centers of the surface of the intermetallic compound, donate a part of their s-electrons to the conduction band of the metal. Because of this at low values of $C_H$, the behavior of hydrogen absorbed by an intermetallic compound is adequately described based on the Ubbelode model,[10] which assumes high diffusion lability of $H^{\delta+}$ atoms or an increase (or, at least, no decrease) in the conductivity of the hydride phase compared to the initial metal. The critical value $C_{H_{cr}}$ or the concentration of the "saturated" solution of hydrogen in the α phase corresponds to the concentration of the oxidizer, *i.e.*, $H^{\delta+}$ atoms, at which the latter oxidize the metal matrix and become acceptors of the electron density by converting into bulky and poorly labile $H^{\delta-}$ ions, and thus depleting the conduction band of the metal. Because of this, the conductivity decreases sharply and the lattice volume increases sharply (stepwise).

In works devoted to experimental studies of the crystal structure of β hydride phases in IMC—$H_2$ systems, it has been noted that the degree of filling of cavities, whose sizes are suitable for the insertion of H atoms, in the crystal lattice-matrix is no more than 50% almost without exception. Apparently, when the degree of filling of cavities with $H^{\delta-}$ ions, which have a rather large effective volume, is higher, the electron deficiency on metal atoms, which form a metal sublattice in the crystal structure of the β hydride phase, should increase, which, apparently, limits its ability to reversibly absorb hydrogen.

An increase in the volume of the crystal lattice by 15—25% leads to an elongation of the interatomic framework M—M bonds (*i.e.*, the bonds that determine the architecture or "design" of the structure) by 8—10%. Such increase in the interatomic distance should be considered as the maximum possible value at which the initial crystal lattice is retained.

The suggested structural model can be considered also as a model, which is based on the concept of the hydride ion, which is severely compressed at 10±5 kbar in the crystal structure of β hydride phases; the effective radius of this ion becomes equal to 0.40—0.50 Å.

Note that the atomic radius of hydrogen in the crystalline monohydrides of Mo, Mn (the NiAs structural type), Ni, and Rh (the NaCl structural type), which can be obtained by "oxidation" of metals by hydrogen at a pressure of several kbars,[16] can be estimated at ~0.60 Å.

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