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Oxidation of Metal Hydrides with Molecular Oxygen

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Abstract—The oxidation of metal hydrides MH_x in the systems $M–H_2–O_2$ (M = Ti, Zr, Sc, Y, V) with molecular oxygen was carried out, and the optimal ranges of temperature and pressure were determined. The resistivity and electron work function for the oxyhydrides synthesized were measured.

Many of structural materials used in atomic, aerospace, and other branches of engineering contain refractory metals such as titanium, zirconium, vanadium, scandium, yttrium, etc. Therefore, physicochemical studies of reactions of these metals or their compounds, in particular, hydrides, with molecular oxygen are always urgent [1].

The $MH_x–O_2$ systems (hereinafter, M = Ti, Zr, V, Sc, Y) were not studied systematically, and only a few papers are devoted to the formation of oxyhydrides of the above metals. Thus, the study of high-temperature oxidation of titanium hydride $TiH_{1.7–2.3}$ with atmospheric oxygen in the polythermal mode is described in [2], where it is shown that the process involves formation of TiH_xO_y and Ti_2O and is completed with the formation of TiO_2 (rutile). Yamanaka *et al.* [3] measured the solubility of hydrogen in titanium and in its oxygen compounds. They showed that the enthalpy of H_2 solution is virtually independent of the oxygen concentration, and the solubility somewhat decreases as the oxygen concentration increases. Hydrogen atoms were assumed to behave as a harmonic oscillator in a titanium matrix [3].

A study of the effect of oxygen on the hydrogenation of oxygen solid solutions in zirconium [4] has shown that the hydrogen content in the samples decreases as the oxygen content increases from 0.6 to 7.3 at.% at 250–900°C and a hydrogen pressure of ~$50–10^5$ Pa.

The system $V–H_2–O_2$ was not studied systematically either: a few papers concerned formation of solid solutions of oxygen in vanadium hydride [5, 6] or in hydrogen bronzes [7].

It seemed reasonable to us to consider in more detail the effect of oxygen and hydrogen on the phase formation in the $M–H_2–O_2$ systems. The results of such study of the systems $TiH_x–O_2$, $ZrH_x–O_2$, and $ScH_2–O_2$ using X-ray analysis and electrophysical measurements were partially presented in [8–11]. Our goal was to prepare the metal oxyhydrides by oxidation of metal di- or monohydrides followed by repeated hydrogenation to ensure the maximal hydrogen content in reaction products and to introduce a possible superstoichiometric amount of hydrogen. The possibility of such introduction is proved, e.g., by the fact that, according to the X-ray analysis [12, 13], two tetrahedral voids in the crystal lattice of TiH_2 are occupied by hydrogen, and the third void of those around a titanium atom, namely, the octahedral void, can probably be occupied by an oxygen atom, which results in formation of an oxyhydride and limits its possible composition to the formula TiH_2O.

Here we report and summarize the experimental data on the synthesis of titanium, zirconium, scandium, yttrium, and vanadium oxyhydrides, and also correlate the data of electrophysical measurements (electron work function and sresistivity) for the resulting oxyhydrides with their phase composition.

The conditions for the oxidation (ranges of pressure, temperatures, and contact duration) of metal hydrides, phase compositions of the reaction products for each system, and unit cell parameters of the solid products are given in the table.

The conditions for the hydride oxidation given in the table allow us to obtain solid reaction products of different phase compositions (from solid solutions of oxygen in a hydride, where their formation is possible, to oxides of the corresponding metals) at relatively insignificant variations of the temperature and pressure in the system, by varying the time of contact of the reactants and the amount of oxygen involved in the reaction.

The oxyhydrides $TiH_{1.46–2.0}O_{0.1–1.4}$ were synthesized by the oxidation of titanium dihydride. The single-phase solid solution $TiH_{1.94–1.99}O_{0.1–0.2}$ crystallizing in the structural type of the initial titanium di-

Conditions and results of the oxidation of metal hydrides

Metal hydride	*p*, MPa	*T*, °C	τ, h	Formula[a]	Phase composition[a]	Unit cell parameters, Å	
						a	*c*
TiH_2	0.3–1.6	500–520	2–5	$TiH_2O_{0.1–1.4}$	$TiH_2O_{0.1–0.35}$	4.442–4.451	–
					TiH_2	4.441–4.450	–
					TiO_2	4.589–4.593	2.957–2.959
ZrH_2	1	300–330	0.1–3	$ZrH_2O_{0.11–1.10}$	$ZrH_2O_{0.11–0.36}$	3.520–3.522	4.442–4.445
					ZrH_2	3.519–3.524	4.442–4.446
					ZrO_2	–	–
ZrH	1	330–350	0.5–3.5	$ZrH_1O_{0.14–1.90}$	Solid solution of hydrogen in α-Zr	3.231–3.235	5.148–5.153
					ZrH_x	4.779–4.835	–
					ZrO_2	–	–
ScH_2	2	500–550	1.5–5	$ScH_2O_{0.23–1.20}$	ScH_2	4.777–4.788	–
					Sc_2O_3	9.829–9.850	–
YH_2	0.9–1.1	210–240	1–4	$YH_2O_{0.1–0.67}$	YH_2	5.198–5.207	–
					Y_2O_3	10.605–10.625	–
$VH_{0.9}$	0.7–1.3	250–400	0.5–3	$VH_{0.9}O_{0.2–1.6}$	$VH_{0.9}$	–	–
					V_2O_3	–	–

[a] Products of oxidation of metal hydrides.

hydride was obtained. When the amount of oxygen in the autoclave is increased, oxygen atoms are introduced into the metal matrix without hydrogen evolution. In this case, the oxygen atoms seem to occupy the corresponding octahedral vacancies. Starting from the composition $TiH_2O_{\sim0.5}$, the increase in the oxygen content in the hydride results in the decomposition of the solid solution with the formation of TiO_2 (rutile) and titanium dihydride, with the unit cell parameters similar to those of the corresponding compounds.

The oxidation of titanium monohydride does not differ in the final result from the oxidation of the dihydride. The oxidized sample remains two-phase after subsequent hydrogenation, and the monohydride phase transforms into the phase of titanium dihydride.

The constancy of the interplanar spacings of the above-mentioned compounds also suggests the absence of appreciable interaction between them in the solid phase.

According to the thermogravimetric data, single-phase samples of the oxyhydride decompose in the polythermal mode to liberate hydrogen in two stages: in the first stage at 570°C the loss of hydrogen is ~20% of its total content, and the major amount of hydrogen is liberated in the second stage (660°C). As the oxygen content in oxyhydrides increases further, the temperatures of these two effects approach each other and untimately merge in a single exoeffect at 640–670°C with the onset of gas evolution at 550°C irrespective of the number of phases in the samples. When two-phase samples are heated, the liberation of hydrogen is accompanied by the decomposition of TiO_2 with the formation of a mixture of various oxide compounds, in which the phase of titanium oxide Ti_2O prevails.

We have synthesizes samples of oxydihydrides and oxymonohydrides $ZrH_2O_{0.11–1.10}$ and $ZrH_{1.0}O_{0.14–1.90}$, respectively, by oxidation of zirconium hydrides. According to the X-ray fiffraction data, at the contact time of 5–40 min the reaction of ZrH_2 with O_2 yields single-phase samples crystallizing in the structural type of the initial ZrH_2 with the unit cell parameters *a* 3.519–3.524 and *c* 4.446–4.442 Å, which do not noticeably differ from the structural characteristics of ZrH_2 [14]. However, when the time of the contact with oxygen increases to 1 h and more, reflections characteristic of monoclinic ZrO_2 appear in the X-ray patterns. Their intensity and number were insufficient to determine the unit cell parameters for this phase. Thus, deep oxidation (330°C, 75–160 min) of zirconium dihydride is accompanied by the formation of two-phase samples. The unit cell parameters of the forming zirconium dihydride practically do not change at various temperatures of subsequent hydrogenation (20–300°C).

According to the thermogravimetric data, single- and two-phase samples decompose similarly to titanium oxyhydrides in the polythermal mode with H_2 liberation in two stages. About 20% of the total amount of hydrogen is liberated at 650–670°C, and the major amount of hydrogen, at 860–870°C. The decomposition product is a mixture of α-Zr with slightly increased lattice parameters and monoclinic zirconium dioxide.

According to the X-ray phase analysis, $ZrH_{1.0}$ is two-phase and contains a phase of α-solid solution of hydrogen in α-Zr (*a* 3.231, *c* 5.149 Å) and cubic zirconium hydride ZrH_x (*a* 4.777 Å). The oxidation of $ZrH_{1.0}$ occurs under conditions similar to those of the dihydride oxidation, up to reaching the composition $ZrH_{1.0}O_{0.40}$, first without changes in the unit cell parameters of the phases, and then, at a deeper oxidation (compositions > $ZrH_{1.0}O_{0.50}$), the unit cell parameter of the cubic crystal lattice of ZrH_x increases, with the α-Zr unit cell parameter remaining virtually unchanged.

Upon repeated hydrogenation of oxidized $ZrH_{1.0}$ samples both at room temperature and at 500°C for 1 h, with gradual cooling of the reaction mixture to ~20°C, zirconium monohydride is converted to the dihydride with the stoichiometric composition, the ZrO_2 phase being preserved.

All products of the oxidation of scandium dihydride are two-phase irrespective of the oxygen content and contain the phases of scandium hydride ScH_2 and scandium oxide Sc_2O_3. Apparent deep oxidation of the initial hydride achievable by increasing the amount of oxygen involved in the reaction is in fact accompanied only by an increase in the content of scandium oxide in the mixture. For example, the increase in the temperature of the reaction of ScH_2 with molecular oxygen from 450 to 550°C reduces the oxidation time from 6.5 to 1.5 h at virtually the same phase composition.

According to the thermogravimetric data, samples of scandium dihydride containing various amounts of the metal oxide decompose on heating in the polythermal mode to 1500°C to evolve H_2 in one stage in the range 900–1130°C and to form powdered metallic scandium, with the Sc_2O_3 phase being preserved. As the oxide content in the mixture increases, the temperature of dihydride decomposition decreases from 1130 to 910°C for a mixture with the composition $ScH_2O_{1.2}$.

Similarly to scandium dihydride, yttrium dihydride reacts with oxygen also with the formation of only two-phase products containing the Y_2O_3 phase in addition to the dihydride. Of all the hydrides studied, yttrium dihydride is characterized by the lowest oxidation temperature (210–240°C).

The X-ray study of oxyhydride samples based on vanadium monohydride has shown that the introduction of even 0.2 oxygen atom per formula unit of $VH_{0.9}$ in vanadium monohydride results in the appearance of reflections characteristic of vanadium oxide V_2O_3 in the X-ray patterns. Thus, all the products of vanadium monohydride oxidation are two-phase.

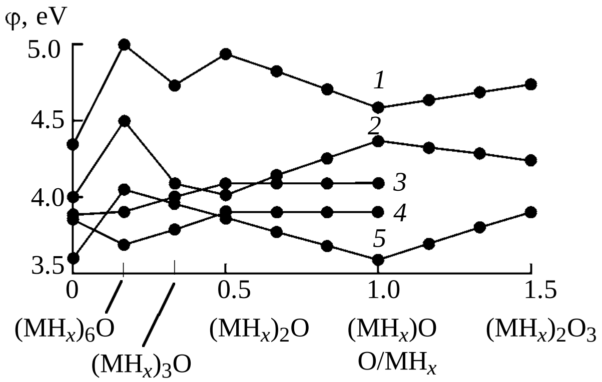
All the samples of vanadium oxyhydride decompose in an inert atmosphere in the polythermal mode to evolve hydrogen at 450°C, which is 30°C higher than the decomposition temperature reported in [15].

Thus, the reactions in all the systems MH_x–O_2 under study are accompanied by the formation of the corresponding metal oxide phase and are not accompanied by an increase in the content of hydrogen in the hydride phase. However, unlike vanadium, scandium, and yttrium hydrides, the introduction of a small amount of oxygen in matrices of titanium and zirconium hydrides results in the formation of intercalation products, solid solutions of oxygen in metal dihydrides having the compositions $TiH_2O_{0.1–0.35}$ and $ZrH_2O_{0.11–0.36}$. The unit cell parameters of the resulting hydrides and oxides of the metals remain virtually unchanged under the conditions of the oxidation and subsequent hydrogenation, which suggests, as mentioned above, the absence of appreciable interactions between the forming phases.

Repeated hydrogenation of the oxidized samples with hydrogen at 20–500°C and hydrogen pressure of 2–3.5 MPa does not increase the hydrogen content in the final oxyhydrides as compared to their initial compositions.

The decrease in the amount of hydrogen in the samples, observed as the oxygen content increases, and the fact that the hydrogen content in the thermal decomposition products (taking into account the weight loss) is the same as that in the initial samples suggest that the oxidation of metal hydrides under the experimental conditions does not promote filling of octahedral oxygen-free voids with hydrogen, i.e., no superstoichiometric metal hydrides are formed upon the oxidation.

For all the systems under study, we have determined voltammetrically the resistivity of metal hydrides and oxyhydrides at 20 and 70°C. We calculated the values and signs of the temperature coefficients of the resistivity (Ψ) from the temperature dependences of the resistivity and also determined



Dependences of the electron work function (φ) on the oxygen content in (*1*) vanadium oxyhydride, (*2*) titanium oxyhydride, (*3*) zirconium oxymonohydride, (*4*) zirconium oxydihydride, and (*5*) yttrium oxydihydride.

from these data the nature of the conductivity of the alloys under study. For the samples with semiconductor conductivity, we determined the carrier sign (*n*- or *p*-type).

The values of Ψ for the system ZrH_2–O_2 [10] show that the conductivity changes from metallic (for the initial ZrH_2) to semiconductor for the samples containing 0.2 oxygen atom/ZrH_2 and more, the absolute value of the temperature coefficient of resistivity growing with an increase in the oxygen content. The variation of Ψ in the system $VH_{0.9}$–O_2 shows that all the samples under study have the semiconductor conductivity to some extent; however, $VH_{0.9}$ and samples of the compositions close to $VH_{0.9}O_{0.3}$ and $VH_{0.9}O_{0.9}$ can be classed with semiconductor metals, whereas the other samples are clearly pronounced semiconductors (*n*-type of conductivity). For some samples, the temperature coefficient of the resistivity appeared to be close to Ψ of V_2O_3, which is known as the electronic semiconductor with the band gap of 0.1 eV [16].

The dependences of the electron work function (φ) on the oxygen content in the coordinates $\varphi = f(O/MH_x)$ are shown in the figure. To examine the isotherms of φ, we invoked the data of X-ray phase analysis and temperature coefficients of the resistivity. A number of characteristic points (extrema and inflections) are observed in the φ isotherms, suggesting the occurrence of phase transitions in the M–H_2–O_2 systems. The first of such points corresponds to the composition $(MH_x)_6O$ of metal suboxides (by analogy with titanium suboxides present in the system Ti–O_2 [17]). A well-defined maximum is present in the systems with V, Ti, and Y in this region of compositions; an isotherm break (curve *3*), in the system $ZrH_{1.0}O_2$; and a minimum (curve *4*), in the system ZrH_2–O_2. As compared to the initial metal hydride, the character of the chemical bond changes in this point from the metal type to the semiconductor type, which is proved by the reversal of the sign of the resistivity temperature coefficient. This phase of suboxyhydride $(MH_x)_6O$ is a stable phase with a variable composition having a certain fraction of ionic (or covalent) bond. As the initial metal hydrides have the metal-type bonding (except for zirconium monohydride showing the semiconductor nature of bonding [10]), the introduction of oxygen atoms into the metal hydride seems to decrease the number of electrons participating in the M–M bond, but their contribution to the M–O bond appears, which results in an increase in the electron work function.

On passing through a characteristic point of $(MH_x)_6O$ and on further increasing the oxygen content in the oxyhydride, its structure starts to rearrange from that of an ordered solid solution (which is especially typical for the systems TiH_2–O_2 and ZrH_2–O_2) to a new stable phase with semiconductor properties, leading to a decrease in φ despite a rise in the M–O bond fraction. In the systems with V and Ti, it can be an $(MH_x)_3O$ phase, and in the system with Y, an $(MH_x)O$ phase. The values of Ψ for the above-indicated systems do not contradict this assumption. The course of the isotherm of the electron work function in the system with Zr is somewhat unusual (to be exact, it is directly opposite to the previous case): As the amount of oxygen in the oxyhydride increases [compared to the composition $(MH_x)_6O$)], the electron work function increases to the value corresponding to the composition $(MH_x)_2O$, which seems to be due to increasing role of the ionic contribution and to a change in the band gap in the semiconductor.

The course of the isotherms of the electron work functions at the oxygen content exceeding that in $(MH_x)_3O$ is different in different systems, though all the oxyhydrides keep the semiconductor nature of bonding.

In the system with V, as the oxygen content is increased above that corresponding to the composition $(MH_x)_3O$, φ starts to grow again, and this growth continues up to the formations of $(MH_x)_2O$. This suggests the occurrence of a new phase transition and an increase in the ionic fraction of the M–O bond. In the system TiH_2–O_2, φ continues to decrease in going from $(MH_x)_3O$ to $(MH_x)_2O$, probably owing to the formation of a new suboxyhydride, with its specific electron work function and band gap, in the framework of the initial phase.

In the region of the $(MH_x)_2O$ compositions, the concentration dependence of the electron work function deviates from a smooth course for all the systems under study, except for the system with yttrium. In the system with vanadium, the second maximum appears here, and in the system with titanium a minimum is observed. Both these peaks can be caused by the formation of a new phase with its specific composition and φ value. In the system with zirconium, in the region of $(MH_x)_2O$ compositions, the isotherm flattens out, suggesting that the phase composition does not change as the oxygen content in the oxyhydride is increased further.

The region of $(MH_x)O$ compositions has also characteristic features: a shallow minimum for the system with vanadium, a deep minimum for the system with yttrium, and a maximum for the system with titanium.

The dependence of φ on the semiconductor properties of oxyhydrides is based on the known fact [18] that, as x values in MO_x semiconductors decrease (defectiveness of the anion sublattice increases), the number of electrons participating in the formation of M–O bonds decreases, but their contribution to M–M bonds increases. The increase in the defectiveness of the cationic sublattice (increasing x) results in the transition from metal properties to semiconductor properties. Similar reasoning seems to be valid for oxyhydrides also. In any case, the results of studying systems with vanadium and yttrium oxyhydrides do not contradict this conclusion.

Comparison of the isotherms of the electron work function for the oxyhydrides studied with the phase diagrams of the $M–O_2$ systems [17, 18] shows that characteristic points in the isotherms clearly correspond to quite certain oxide phases, which clearly confirms the presence of oxyhydride phases in $M–H_2–O_2$ systems, in particular, of the phases with the compositions $(MH_x)_6O$, $(MH_x)_3O$, and $(MH_x)_2O$.

EXPERIMENTAL

Metal dihydrides MH_2 were obtained by a procedure described in [19]; titanium and zirconium monohydrides, by heating of the corresponding dihydrides with continuous evacuation [8, 10]. We subjected vanadium monohydride to oxidation, as vanadium dihydride has a high dissociation pressure (~0.2 MPa at 20°C) and it decomposes under normal conditions to the monohydride $VH_{0.9}$.

The oxidation of metal hydrides MH_x with molecular oxygen of 99.6–99.8% purity was carried out in a laboratory high-pressure installation by the technique from [8]. Metal hydrides with particle size of 50 μm obtained by hydride dispersion were oxidized. The oxidation of powdered metal hydrides with a smaller particle size is uncontrollable and is accompanied by significant heat evolution. Owing to the high reactivity of yttrium hydride, it was oxidized with a 1:1 oxygen–argon mixture.

The technique of chemical and thermogravimetric analyses, measurement of electrophysical properties, and preparation of samples for the analysis and measurements are described in detail in [9].[1]

The X-ray studies of the initial hydride phases and products of their reactions with oxygen were made on an automatic complex consisting of an ADP-1 diffractometer (CuK_α [9] or CrK_α radiation) and a controlling computer. The error in determination of the unit cell parameters did not exceed 0.004 Å.

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