In the determination of $\Delta H^\circ_H$, $\Delta S^\circ_H$, and $\gamma$ use was made of experimental data referring to the hydrogen mole fraction range 0.02–0.44 and the temperature range 800–1200$^\circ$K. However, the character of the above expressions relating these quantities to temperature enables Eq. (8) to be extrapolated to higher temperatures (right up to the melting point of titanium).

Equation (8) was employed for calculating hydrogen concentrations in the solution at temperatures of 1000–1900$^\circ$K for given compositions of the Ti–H–Ar system and gaseous phase pressures (Figs. 1–3). As can be seen, the greatest changes in the composition of the solution take place in the range 1000–1600$^\circ$K, while at higher temperatures the solution composition changes only slightly both with temperature and with composition of the system. As regards quantitative results, it may be concluded that at 1800–1900$^\circ$K and atmospheric pressure of the gaseous phase the degree of hydrogen desorption attained is the same as at $T = 1000$–1100$^\circ$K and $P = 10$–100 Pa [2].

LITERATURE CITED


REACTION OF A SINTERED INTERMETALLIC COMPOUND Ti$_2$Ni WITH HYDROGEN

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The sorption properties of intermetallic compounds capable of accumulating hydrogen depends to a large extent on their previous history, especially as such compounds are formed by high-activity metals. In [1, 2] it is shown that, compared with specimens produced by melting, sintered intermetallic compounds are characterized by higher sorption and desorption rates and slightly higher hydrogen capacity. Such properties in relation to hydrogen are ensured by the well-developed, active surfaces of sintered specimens. This makes it possible to decrease the intensity of the activation of material before the beginning of hydrogen sorption, which is a labor- and time-consuming operation, and in some cases dispense with it altogether.

The intermetallic compound Ti$_2$Ni – a hydrogen accumulator operating at comparatively high temperatures (sorption–desorption temperatures of 200–300°C) – is attracting considerable attention because of its relatively low cost, ease of preparation, and satisfactory hydrogen sorption characteristics. The intermetallic compound Ti$_2$Ni produced by the melting technique has already been investigated in some detail [3–6]. The presence of oxygen in this compound has a pronounced effect on its hydrogen sorption properties [4–6].

In the present work a study was made of the sorption properties of the intermetallic compound Ti$_2$Ni produced by sintering a mixture of titanium and nickel powders. The specimens were ~10-mm-diameter, ~10-mm-high cylinders of ~30% porosity. Chemical analysis showed that the oxygen content of the Ti$_2$Ni was 0.7 wt.%, corresponding to the arbitrary formula Ti$_2$NiO$_{0.07}$. It was established by x-ray diffraction that the specimens had a single-phase fcc structure with a lattice constant $a = 1.1324$ nm – a value matching
that given in [7]. Control tests demonstrated that 120-day storage in air did not affect the sorptive capacity of the specimens. The sorption properties of Ti$_2$Ni were studied, using a Sieverts-type apparatus, in the temperature range 293-1173 K at hydrogen pressures of 0.1-4 MPa. The majority of the specimens used in tests were not crushed.

The heating of a specimen to a suitable temperature (1173 K) in a dynamic (flow-type) vacuum (13 Pa) activated its surface. In the range 673-1173 K the sorption process came to an end after 5-10 min (Fig. 1). With fall in temperature the time taken to reach an arbitrary equilibrium became longer, and at room temperature was about 2 days. Under conditions of sorption and desorption on one and the same specimen at room temperature its hydrogen capacity* grew from 90 after the first cycle to 103 cm$^3$/g after the seventh (Fig. 1). At other temperatures investigated the polytherm were exactly reproduced in all consecutive cycles. The maximum hydrogen content of the hydride recorded at a pressure of 0.1 MPa was 103 cm$^3$/g, corresponding to the arbitrary formula Ti$_2$NiO$_{0.07}$H$_{1.45}$. It was found that, when hydrogen was admitted after a specimen had been heated in the dynamic vacuum to 1173 K and then cooled to room temperature, sorption commenced at once, but was very slow (only 36 cm$^3$/g after 48 h).

In the hydrogenation of a crushed specimen (particle size 80 μm) the limiting sorption capacity was much smaller, 34 cm$^3$/g, which was indicative of a strong influence of surface contamination with oxygen and nitrogen, resulting in the formation of a layer impeding the penetration of hydrogen into particles (similar findings are reported in [4, 5]). Under these conditions, as would be expected in view of the large solubility of oxygen and nitrogen in titanium and its compounds [8], the surface experienced no activation even during heating to high temperatures in the dynamic vacuum.

Specimens of the intermetallic compound Ti$_2$NiO$_{0.07}$ were exposed to hydrogen also at high pressures (up to 4 MPa) during cooling from temperatures of 673-734 °K. Their hydrogen capacity determined during dehydrogenation by the volumetric method was 129-134 cm$^3$/g. A chemical analysis of a specimen after dehydrogenation revealed the presence of residual hydrogen (24 cm$^3$/g) in it. Thus, the full hydrogen absorption capacity of such specimens was 155 cm$^3$/g, corresponding to the composition Ti$_2$NiO$_{0.07}$H$_{1.45}$. The limiting hydrogen sorption capacity in cyclic hydrogenation and dehydrogenation was reproduced from cycle to cycle.

Experiments on the decomposition of the hydrides Ti$_2$NiO$_{0.07}$H$_{1.45}$ and Ti$_2$NiO$_{0.07}$H$_{1.8}$ were conducted in a closed evacuated volume at a residual pressure of 13 Pa under conditions of continual heating at a rate of 40 deg K/min. In Fig. 2 decomposition curves showing the dependence of hydrogen concentration on temperature (curves 2 and 5) are compared with data reported in [4] (curves 1, 3, and 4), where hydrides decomposed in a

*Throughout this article hydrogen capacity is expressed in cubic centimeters of gaseous hydrogen under normal conditions, referred to 1 g of the starting sorbent.