HYDROGEN SORPTION IN B.C.C. VANADIUM ALLOYS

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Vanadium dihydride (VH_2) has the maximal among the known hydrides volumetric hydrogen capacity (up to 0.16 g/cm^3 or 2.25 times more than the density of liquid hydrogen), as well as high enough hydrogen weight capacity (3.78 wt.%). About 50% of this hydrogen reversibly absorbs / desorbs under acceptable conditions: at room temperature and pressure more than 1 bar. The absorption / desorption are characterized by higher (as compared to intermetallic hydrides with similar characteristics) enthalpy and entropy. It allows to realize more efficiently the processes of hydrogen thermal sorption compression or low-potential heat management using the VH – VH_2 transition.

The practical implementation of VH_2 is hampered by a number of difficulties including slow formation kinetics, high sorption hysteresis, limited possibility to control the temperature dependence of hydrogen pressure starting from requirements of the specific applications. Recently the growing R&D activities to solve these problems are observed. In particular, it was shown that vanadium – titanium alloys with small additives of transition elements (Cr, Mn, Ni, etc.) have the improved hydrogen sorption characteristics. In some works it was reported about improvement of hydriding kinetics of vanadium in the alloys with Zr additives.

In this work there were investigated hydrogen sorption properties of multi-component alloys of the composition $V_{92.5-x-y}Zr_{7.5}Ti_{x+7.5-y}M_y$, where M=Cr, Mn, Fe, Co, Ni; x=0, 10 and y=0, 7.5. The selected ratio of the components approximately corresponds to the limit of the single-phase region of the b.c.c. solid solution at T~1000 °C. The alloys were prepared by arc melting in the argon atmosphere and then were annealed at 1100 °C during 50 hours.

According to X-ray diffraction studies, all the starting alloys contain the major b.c.c. phase, space group #229 $\left(Im\bar{3}m\right)$, a=3.025–3.040 Å.

Before hydrogen sorption measurements, a sample of the alloy (1–2 bulk pieces, total weight 0.8–1.5 g) was activated by vacuum heating at 450 °C during 1 hour followed by saturation with hydrogen gas at P~10 bar and room temperature. The operations have been repeated until reproducibility of the hydrogen sorption capacity. The data on hydrogen sorption properties of the studied alloys are presented in the Table. It can be seen that all the alloys have the hydrogen sorption capacity corresponding to H/M=1.6–1.8 (330–375 cm^3/g STP), and the reversible capacity at T<100 °C and P>0.1 bar is 50 to 60% of the total value. The rest hydrogen can be desorbed in vacuum at 180–230 °C.

The multicomponent V–Zr–Ti–M alloys have the excellent hydrogen sorption kinetics: the complete hydrogenation takes no more than 20 minutes already on the first cycle, and no more than 5 minutes on the consequent cycles. The samples completely saturated with hydrogen mainly contain the f.c.c. VH_2-like phase, space group #225 $\left(Fm\bar{3}m\right)$, the lattice period depending on the composition of the starting alloy varies within a=4.256–4.295 Å.

Alloy	H sorption capacity				Time of 80% hydriding at the 1st activation cycle, min.	Number of cycles before reproducing H_2 sorption
	Total		Reversible			
	H/M	cm^3/g STP	H/M	cm^3/g STP		
$V_{75}Ti_{17.5}Zr_{7.5}$	1.76	367.4	0.90	189.3	2.5	1
$V_{92.5}Zr_{7.5}$	1.65	343.1	0.81	168.2	75	4
$V_{75}Ti_{10}Zr_{7.5}Cr_{7.5}$	1.79	370.3	1.09	224.7	2.0	1
$V_{75}Ti_{10}Zr_{7.5}Mn_{7.5}$	1.80	374.0	1.10	228.5	5.5	1
$V_{75}Ti_{10}Zr_{7.5}Fe_{7.5}$	1.59	328.9	0.76	156.5	12.0	1
$V_{75}Ti_{10}Zr_{7.5}Co_{7.5}$	1.67	344.1	0.90	185.4	8.5	1
$V_{75}Ti_{10}Zr_{7.5}Ni_{7.5}$	1.56	321.9	0.88	181.1	16.5	1

The measurements of the PCT relations for the systems of the alloys under investigation with hydrogen gas (T=30–120 °C) have shown the essential influence of the substituting components on the thermodynamics of the $VH_{\sim 2} \leftrightarrow VH_{\sim 1}$ transition. So, at T=60 °C the hydrogen desorption equilibrium pressure for the upper plateau is about 10 bar for the $V_{92.5}Zr_{7.5}$–H_2 system and about 0.8 bar for $V_{75}Ti_{17.5}Zr_{7.5}$–H_2. The corresponding values for the tetrad alloys have the intermediate values within the indicated range. So, by variation of a small additive of the M-component in V–Zr–Ti–M it is possible to change hydrogen equilibrium pressure by more than order of magnitude.

On the basis of results obtained, it is possible to conclude that the multi-component b.c.c. alloys on the vanadium basis with additives of Ti and the metal of VI–VIII groups are the highly-efficient hydrogen sorbents which can be used for the creation of the compact metal hydride hydrogen storage units, thermal sorption compressors and other applications.