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Reaction of Hydride Phases of Zirconium Intermetallic Compounds with Molecular Nitrogen

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Abstract—Reaction of hydride phases of zirconium intermetallic compounds with molecular nitrogen was studied at 293 and 973 K and nitrogen pressure of 10 MPa. At 293 K, hydride–nitride phases crystallizing in the structural types of the initial hydride phases are formed in all cases, whereas at 973 K finely dispersed heterophase mixtures of zirconium, molybdenum, and vanadium nitrides with 3*d* transition metals or mixtures of zirconium nitride with vanadium, molybdenum, chromium, and manganese nitrides are formed.

In [1–4], we studied the reaction of binary and pseudobinary zirconium intermetallic compounds with hydrogen. We found that these compounds are not broken down under the action of hydrogen but form the corresponding hydride phases. The hydride phases based on ZrV_2, $ZrMo_2$, ZrVFe, ZrVCo, ZrVNi, $ZrCr_2$, $ZrMn_2$, ZrMoFe, and ZrNi crystallize in the structural types of the initial intermetallic compounds, and the ZrCo crystal lattice (CsCl type) rearranges into an orthorhombic lattice.

We showed previously that the hydride phases based on rare-earth and 3*d* transition metals are more reactive toward nitrogen than the initial intermetallic compounds, and the two-step transformation intermetallic compound → hydride phase of the intermetallic compound → nitride phase can be performed easier than the single-step transformation intermetallic compound → nitride phase [5].

In view of this fact, we examined here the reaction with molecular nitrogen of hydride phases of zirconium intermetallic compounds crystallizing in the structural types of $MgCu_2$, $MgZn_2$, CsCl, and CrB. This paper continues our previous studies [5–7].

The results of experiments on reaction of zirconium hydride phases with molecular nitrogen (10 MPa) at 293 and 973 K are listed in Table 1. As seen from these data, at room temperature, irrespective of the chemical composition of the initial hydride phases and structural type of their lattices, hydride–nitride derivatives are formed with the unit cell parameters virtually equal to those of the corresponding hydride phases. That is, uptake of a small amount of nitrogen affects the structure of the hydride phases insignificantly. The specific surface areas measured after removal of hydrogen and nitrogen from hydride and hydride–nitride phases by high-vacuum treatment are consistent with this conclusion.

At the reaction temperature increased to 973 K, the reaction occurs differently (Table 1). As the free energies of formation of zirconium, vanadium, molybdenum, chromium, and manganese nitrides are close under these conditions [8], in the hydride phases derived from the intermetallic compounds ZrV_2, $ZrMo_2$, $ZrCr_2$, and $ZrMn_2$, the components of these phases are nitrided simultaneously in the proportions corresponding to the composition of the initial hydride phase. If the free energy of formation of a metal nitride is positive or strongly differs from those of nitrides of the other metals constituting the intermetallic compound, one or two metal components of a hydride phase of a zirconium intermetallic compound can react with nitrogen selectively. This is the case in reaction of molecular nitrogen with metallic components of the hydride phases derived from intermetallic compounds ZrVT (T = Fe, Co, Ni), ZrMoFe, ZrCo, and ZrNi. In the process, the specific surface area of the solid phase noticeably increases owing to formation of nitride and metallic phases. It should be noted that the unit cell parameters of these phases are in good agreement with published data for the individual compounds [9], suggesting the absence of noticeable solid-state interaction between these phases at 973 K and N_2 pressure of 10 MPa.

Thus, reactions of hydride phases of binary and pseudobinary zirconium alloys with molecular nitrogen can be described by the following equations:

$$ZrM_mTH_x \xrightarrow[N_2]{293\text{ K, }10\text{ MPa}} ZrM_mTH_xN_y,$$

$$ZrM_mTH_x \xrightarrow[N_2]{293\text{ K, }10\text{ MPa}} ZrN + T + mMN,$$

M = V, Mo, Cr, Mn; T = Fe, Co, Ni; $x = 4.7–1.1$; $y = 0.01–0.03$; $m = 1, 2$.

Table 1. Reaction of hydride phases of zirconium intermetallic compounds with nitrogen (10 MPa) at 293 (100 h) and 973 K (10 h)

Hydride phase	Reaction conditions		Phase composition of reaction products	Unit cell parameters, Å			S, m^2 g^{-1}
	T, K	τ, h		a	b	c	
$ZrV_2H_{4.8}$	293	100	$ZrV_2H_{4.7}N_{0.01}$	7.951	–	–	0.22
	973	10	ZrN	4.538	–	–	0.55
			+ VN	4.137	–	–	
$ZrVFeH_{4.0}$	293	100	$ZrVFeH_{4.0}N_{0.02}$	5.465	–	8.921	0.29
	973	10	ZrN	4.537	–	–	0.75
			+ VN	4.135	–	–	
			+ α-Fe	2.865	–	–	
$ZrVCoH_{4.0}$	293	100	$ZrVCoH_{3.9}N_{0.02}$	5.413	–	8.835	0.25
	973	10	ZrN	4.536	–	–	0.79
			+ VN	4.138	–	–	
			+ Co	2.505	–	4.082	
$ZrVNiH_{2.8}$	293	100	$ZrVNiH_{2.8}N_{0.01}$	5.395	–	8.796	0.23
	973	10	ZrN	4.539	–	–	0.82
			+ VN	4.133	–	–	
			+ Ni	2.524	–	–	
$ZrCoH_{3.0}$	293	100	$ZrCoH_{2.9}N_{0.03}$	3.537	10.478	4.302	0.19
	973	10	ZrN	4.535	–	–	0.43
			+ Co	2.506	–	4.071	
$ZrNiH_{3.0}$	293	100	$ZrNiH_{3.0}N_{0.02}$	3.529	10.480	4.305	0.21
	973	10	ZrN	4.540	–	–	0.47
			+ Ni	2.525	–	–	
$ZrCrH_{2.6}$	293	100	$ZrCr_2H_{2.5}N_{0.02}$	5.333	–	8.712	0.20
	973	10	ZrN	4.538	–	–	0.49
			+ CrN	4.150	–	–	
$ZrMo_2H_{1.4}$	293	100	$ZrMo_2H_{1.3}N_{0.02}$	7.691	–	–	0.25
	973	10	ZrN	4.537	–	–	0.61
			+ Mo_2N	4.166	–	–	
$ZrMoFeH_{2.4}$	293	100	$ZrMoFeH_{2.3}N_{0.02}$	5.389	–	8.809	0.24
	973	10	ZrN	4.539	–	–	0.68
			+ Mo_2N	4.170	–	–	
			+ α-Fe	2.866	–	–	
$ZrMn_2H_{1.0}$	293	100	$ZrMn_2H_{1.1}N_{0.03}$	5.040	–	8.288	0.25
	973	10	ZrN	4.541	–	–	0.57
			+ Mn_3N_2	4.198	–	4.035	

EXPERIMENTAL

The initial alloys were prepared by fusion of the metals: iodide-refined zirconium (99.99%), molybdenum (98.9%), cobalt (99.3%), iron (99.91%), nickel (99.99%), electrolytic vanadium (99.9%), and electrolytic chromium (99.7%). The metals were fused on a water-cooled copper hearth of an electric arc furnace with an unconsumable tungsten electrode at an argon (high purity) pressure of ~0.2 MPa. The weighing of the samples after fusion showed that deviation from the initial composition was insignificant (within 0.05 wt %). The samples were remelted three times to obtain single-phase alloys. Homogenizing annealing was performed at 1073 K for 1200 h in evacuated quartz ampules with subsequent quenching in ice-cold water. To prevent the reaction of the alloys with quartz, they were wrapped in a molybdenum foil. Titanium turnings were used as getter to remove residual oxygen from the ampule. According to neutron activation analysis, the oxygen content in the samples did not exceed 3.5×10^{-2}%.

Table 2. Characteristics of zirconium intermetallic compounds and their hydrogenation products

Compound	Structural type	Unit cell parameters, Å			S, $m^2 g^{-1}$
		a	b	c	
ZrV_2	$MgCu_2$	7.442	–	–	
$ZrV_2H_{4.8}$	$MgCu_2$	7.954	–	–	0.23
ZrVFe	$MgZn_2$	5.048	–	8.485	
$ZrVFeH_{4.0}$	$MgZn_2$	5.463	–	8.924	0.27
ZrVCo	$MgZn_2$	5.041	–	8.233	
$ZrVCoH_{4.0}$	$MgZn_2$	5.410	–	8.838	0.25
ZrVNi	$MgZn_2$	5.011	–	8.197	
$ZrVNiH_{2.8}$	$MgZn_2$	5.393	–	8.798	0.24
ZrCo	CsCl	3.198	–	–	
$ZrCoH_{3.0}$	CrB	3.532	10.481	4.298	0.21
ZrNi	CrB	3.260	9.943	4.091	
$ZrNiH_{3.0}$	CrB	3.525	10.483	4.303	0.19
$ZrCr_2$	$MgZn_2$	5.104	–	8.275	
$ZrCr_2H_{2.6}$	$MgZn_2$	5.335	–	8.710	0.22
$ZrMo_2$	$MgCu_2$	7.546	–	–	
$ZrMo_2H_{1.4}$	$MgCu_2$	7.694	–	–	0.25
ZrMoFe	$MgZn_2$	5.129	–	8.443	
$ZrMoFeH_{2.4}$	$MgZn_2$	5.387	–	8.810	0.28
$ZrMn_2$	$MgZn_2$	5.042	–	8.285	
$ZrMn_2H_{1.0}$	$MgZn_2$	5.491	–	8.775	0.26

The X-ray diffraction study of the initial alloys and products of their interaction with hydrogen and nitrogen was performed with a computer-controlled ADP-1 diffractometer (CuK_α radiation). The unit cell parameters were determined with an accuracy of 0.004 Å for the initial intermetallic compounds and 0.008 Å for the reaction products. For the intermetallic compounds ZrV_2 and $ZrMo_2$, we confirmed the $MgCu_2$ structure; for ZrVFe, ZrVCo, ZrVNi, and $ZrCr_2$, the $MgZn_2$ structure; for ZrCo, the CsCl structure; and for ZrNi, the CrB structure (Table 2); their unit cell parameters are in good agreement with published data [9].

The specific surface areas of samples were determined by the BET method from low-temperature adsorption of Kr after heating at 620 K and 5×10^{-3} Pa.

The hydrogen content in the reaction products was determined by the standard procedure (combustion in an oxygen flow), and the nitrogen content, by the Kjeldahl and Dumas methods.

Reactions of zirconium intermetallic compounds with hydrogen and nitrogen were studied by standard procedures on a laboratory high-pressure installation.

All manipulations with the reaction products, including sampling, were performed in an argon atmosphere.

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