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New Phases in the Mg–Ta–H_2 System at High Quasi-hydrostatic Pressures

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Abstract—The Mg–Ta–H_2 system was investigated at quasi-hydrostatic pressures from 4 to 5 GPa and temperatures from 900 to 1000°C. X-ray diffraction studies indicate the formation of three new hydrides: (Ta,Mg)H_x (solid solution of magnesium hydride in tantalum hydride), (Mg,Ta)H_2 (solid solution of tantalum hydride in α-MgH_2), and $Mg_xTa_yH_z$.

INTRODUCTION

Mixed hydrides with the general formula $M_xT_yH_n$, where M is an alkali or alkaline-earth metal and T is a transition metal, have not yet been extensively studied.

A salient feature of the ternary hydrides containing a Group VIII transition metal is the formation of ionic complexes with strong, covalent H–T bonding. In most cases, such hydrides can be prepared by hydrogenating the appropriate alloys or elemental mixtures. At the same time, high-pressure synthesis in the Mg–Mn–H_2, Ca–Ni–H_2, and Ca–Co–H_2 systems was found to yield new hydrides, which cannot be prepared by hydrogenating metals [1, 2].

In this paper, we describe the phase relations in the MgH_2–$TaH_{0.9}$ system at high quasi-hydrostatic pressures.

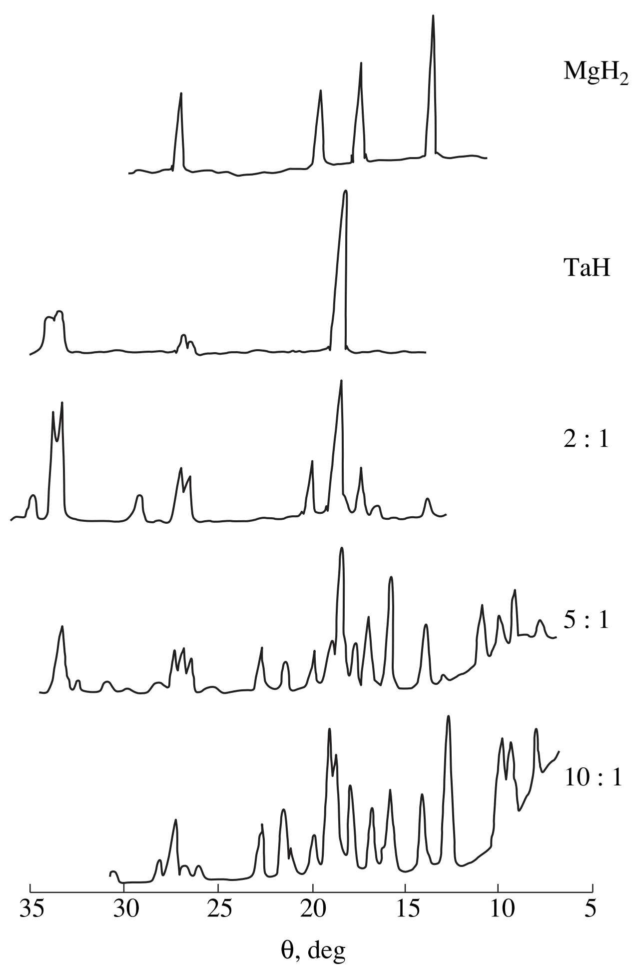
EXPERIMENTAL

Magnesium and tantalum hydrides were prepared by reacting Mg and Ta metals with pure hydrogen at pressures from 5 to 10 MPa and temperatures from 300 to 800°C. The reaction mixtures, prepared by thoroughly grinding appropriate ratios of the constituent hydrides in an agate mortar, were pressed into disks and placed in a ≃1-cm^3 lens-shaped catlinite anvil cell. Dry sodium chloride was used as a pressure-transmitting medium, isolating the sample from the graphite heater. The phase composition of the samples was determined by x-ray diffraction (XRD) analysis (DRON-2 powder diffractometer, CuK_α radiation).

RESULTS AND DISCUSSION

To study high-pressure phase relations in the MgH_2–$TaH_{0.9}$ system, we prepared mixtures with MgH_2 : $TaH_{0.9}$ molar ratios of 1 : 1, 2 : 1, 3 : 1, 5 : 1, and 10 : 1. The samples were held at 4–5 GPa and 900–1000°C for 1–3 h.

The XRD patterns illustrating the observed transformations are shown in the figure. Note that in none of our experiments was full conversion attained, and all of the samples contained appreciable amounts of MgH_2



XRD scans of the constituent hydrides and the reaction products obtained at MgH_2 : $TaH_{0.9}$ = 2 : 1, 5 : 1, and 10 : 1.

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and $TaH_{0.9}$. For this reason, the compositions of the new phases could not be determined. Analyses for hydrogen by high-temperature vacuum extraction showed that its content was not altered by high-pressure processing. This finding lends support to the conclusion that, at high pressures, the thermal stability of binary hydrides is higher [3].

According to earlier results, the Ta–H_2 system contains no hydride phases up to p_{H_2} = 1 GPa [4]. Magnesium hydride undergoes polymorphic transformations under high quasi-hydrostatic pressures into α-MgH_2 (α-PbO_2 structure type) and the hexagonal (pseudocubic) phase γ-MgH_2 [3, 5].

As follows from our XRD data (figure), after high-pressure processing, the sample with $MgH_2 : TaH_{0.9}$ = 2 : 1 contains an fcc phase with $a = 4.452 \pm 0.002$ Å (Table 1).

The fcc lattice is characteristic of the higher vanadium and niobium hydrides. It seems likely that, under high pressures, magnesium hydride partially dissolves in tantalum hydride to form $(Ta,Mg)H_x$ ($x > 1$) with the CaF_2 structure.

The same is evidenced by the XRD data for the samples with $MgH_2 : TaH_{0.9}$ = 3 : 1 and 10 : 1. In this case, however, tantalum hydride dissolves in the α-form of magnesium hydride. The Ta atoms are likely to be ordered in the structure of α-MgH_2, as evidenced by the presence of the 010, 001, and 100 superlattice reflections (Table 2).

At $MgH_2 : TaH_{0.9}$ = 3 : 1, the lattice parameters of $(Mg,Ta)H_2$ are a = 4.519(2) Å, b = 5.495(1) Å, c = 4.670(2) Å, and V = 115.9 Å^3; at $MgH_2 : TaH_{0.9}$ = 10 : 1, we obtained a = 4.577(3) Å, b = 5.542(2) Å, c = 4.667(2) Å, and V = 118.4 Å^3 (V = 121.5 Å^3 for α-MgH_2). Thus, the dissolution of tantalum hydride in magnesium hydride reduces the unit-cell volume, in accordance with the metallic radii of Mg and Ta.

The XRD pattern from the sample with $MgH_2 : TaH_{0.9}$ = 5 : 1 (figure) is more difficult to interpret. At this stage, we suppose that a new mixed hydride of composition $Mg_xTa_yH_z$ was obtained.

According to preliminary data, $Mg_xTa_yH_z$ crystallizes in orthorhombic symmetry with a = 5.066(2) Å, b = 9.043(2) Å, and c = 4.737(1) Å (Table 3).

In conclusion, note once again that our inferences regarding the structure of the new phases are only tentative. What is established with certainty is that new phases form in the Mg–Ta–H_2 system at high quasi-hydrostatic pressures. Additional, indirect evidence of this is that the samples turn light brown, and the depth of coloration increases in going from $MgH_2 : TaH_{0.9}$ = 5 : 1 to 10 : 1 (which, however, can also be due to the decrease in the amount of unreacted tantalum hydride, which has a black color).

Table 1. XRD data for $(Ta,Mg)H_x$

hkl	d_{obs}, Å	$1/d^2_{obs} \times 10^4$	$1/d^2_{calc} \times 10^4$	*I*, %
111	2.562	1522	1517	100
200	2.224	2025	2022	58
220	1.573	4044	4045	29.2
311	1.345	5564	5562	20.85
420	0.994	10105	10112	12.5

Table 2. XRD data for $(Mg,Ta)H_x$

hkl	d_{obs}, Å	$1/d^2_{obs} \times 10^4$	$1/d^2_{calc} \times 10^4$	*I*, %
010	5.608	318	326	26
001	4.695	454	459	47
100	4.599	473	477	68
110	3.548	795	803	100
111	2.822	1255	1262	68
020	2.793	1299	1300	22
021	2.374	1775	1770	79
200	2.298	1894	1900	53
220	1.758	3234	3225	9
130	1.714	3404	3408	11
202	1.634	3745	3746	14
222	1.410	4097	5003	4

Table 3. XRD data for $Mg_xTa_yH_z$

hkl	d_{obs}, Å	$1/d^2_{obs} \times 10^4$	$1/d^2_{calc} \times 10^4$	*I*, %
100	5.096	385	390	28
020	4.529	488	498	100
110	4.439	507	512	56
011	4.133	585	576	94
120	3.401	864	872	11
021	3.255	944	940	11
130	2.629	1447	1442	20
200	2.536	1555	1559	50
002	2.362	1793	1782	64
220	2.217	2035	2048	15
022	2.108	2250	2265	44
221	1.998	2506	2493	60
231	1.791	3119	3110	11
202	1.728	3350	3341	31

To determine the structure and composition of the high-pressure hydrides, neutron diffraction studies are needed.

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