HYDRIDES OF INTERMETALLIC COMPOUNDS CONTAINING PLATINUM-GROUP METALS

Padurets L.N., Kuznetsov N.T., Shilov A.L.*
Institute of General and Inorganic Chemistry of RAS
Leninskii prospekt 31, Moscow, 119991, Russia
*Fax: ++7 (095) 9541279 E-mail: ashilov@rambler.ru

It is well known that chemistry of metal hydrides starts from the work of Graham. In 1866 he discovered the absorption of hydrogen by palladium resulting in $PdH_{0.6}$. Another platinum-group metals (PM) do not absorb hydrogen at moderate conditions (although in highly dispersed state they can absorb up to 0.1H/M). Only Rh forms hydride $RhH_{\sim 1}$ at ca. 1 GPa.

Investigations of interaction of binary intermetallic compounds (IMCs), containing PM, with hydrogen are summarized in the Table. Limiting hydrogen contents obtained at hydrogen pressure up to 10 MPa are presented.

$YRu_2H_{3.3}$		$YPdH_{3.1}$	
$LaRu_2H_{4.5}$	$LaRh_2H_{4.9}$		
$CeRu_2H_{5.2}$			
$NdRu_2H_{5.5}$			
$SmRu_2H_{4.6}$			
	$EuRh_2H_{5.5}$	$EuPdH_{\sim 1}$ $EuPd_2H_{1.7}$	
$GdRu_2H_{3.7}$	$GdRh_2H_{3.3}$	$Gd_7Pd_3H_{10}$ $Gd_3Pd_2H_5$	
$DyRu_2H_{\sim 3}$	$DyRh_2H_{\sim 3}$		
$HoRu_2H_{4.2}$			$HoPtH_2$
$ErRu_2H_{3.6}$			
		$YbPdH_{2.7}$	
$ThRu_2H_5$		Th_2PdH_6 $ThPdH_4$	
		Ti_2PdH_2	
		$Zr_2PdH_{2.7}$	
	$Hf_2RhH_{2.2}$	$Hf_2PdH_{1.9}$	

Such IMCs as $ScRu_2$, $NdIr_2$, LuPd, $GdPd_2$, $LaPt_2$, $LaPt_5$, and $ZrPd_2$ do not absorb hydrogen under these conditions or absorb only 0.1-0.3 H/mol). $LaPt_5$ forms hydrides at 20-105 MPa.

An interesting circumstance may be noted: alloys of metals, each of them is hydride-forming (RE, Ti, Pd), absorb less hydrogen than the sum of corresponding pure metals or do not absorb hydrogen at all (sf. also $LiPtH_{0.66}$ and $LiPdH_{0.82}$). In other hand, pure Ru does not absorb hydrogen even at 7 GPa, but it is actively "entrained" in hydriding being the component of IMCs.

Such hydrides as $Ca(Sr)_2Ir(Rh)H_5$, $Ca(Sr)_2RuH_6$, $Eu(Yb)_2RuH_6$, Eu_2IrH_5 are also known. However, they are not the insertion phases, obtained by hydrogen interaction with IMCs (corresponding IMCs do not exist at all). These compounds can be obtained by the reaction of binary hydrides RH_2 with dispersed PM in hydrogen at high temperatures.

Interaction of ternary alloys containing PM with hydrogen is relatively poorly studied. It was shown that the substitution of 20% Ni by Pd in $LaNi_5$ decreases the absorption capacity twice and increases the hydrogen dissociation pressure (at 298 K) from 0.25 to 7 MPa. Hydrides of ternary Ru-containing alloys were obtained and studied by authors: $SmFe_{2-x}Ru_xH_{\sim 4}$, $SmCo_{2-x}Ru_xH_{\sim 4}$, $SmCo_{1.8}Ru_{1.2}H_{4.5}$, $SmNi_{0.85}Ru_{1.15}H_4$, $SmNi_{1.4}Ru_{1.6}H_{3.3}$, $ErFe_{2-x}Ru_xH_{3-5}$, $ErCo_{3-x}Ru_xH_{3.5-4}$.

The results of X-ray investigations of hydrides can be summarized as follow. In most cases hydriding results in simple expansion of the metallic matrix with the volume increase (dV) in the range 10-30%. For $LaRh_2$, $GdRh_2$, Ti_2Pd, $SmCo(Ni)_{3-x}Ru_x$ hydriding is accompanied by the distortion of the initial crystal structure. In the case of $NdRu_2$ and $SmRu_2$ hydrogen induces the polymorphic $MgCu_2$-to-$MgZn_2$ transformation. For ternary Sm-based Laves-phases the hydrogen-induced amorphyzation occurs. The formation of YbPd-, $EuRh_2$-, and $CeRu_2$-hydrides is accompanied by the lowering of RE valence state: from 3 to 2 for Yb and Eu, from 4 to 3 for Ce. For these hydrides dV-values are extremely high.

Data concerning the values of the heat of formation are limited by hydrides based on $RERu_2$ (-dH = 46-65 kJ/mol H_2), $RERh_2$ (-dH = 44-49 kJ/mol H_2), and YbPd (-dH = 87 kJ/mol H_2).

Thermal stability was studied for hydrides of binary and ternary Ru-containing alloys. Part of these hydrides desorbs hydrogen reversibly (in one- or multi-stage manner). Another hydrides (based on $LaRu_2$, $NdRu_2$, and some ternary Laves-phases), after the desorption (complete or partial) of hydrogen, decompose into binary REH_2 and phases enriched by d-metals (hydrogenolysis process).