JOURNAL OF SOLID STATE CHEMISTRY 16, 209–210 (1976)

NOTE

Studies of Hydride Formation and Superconductivity in Hydrides of Th–Pd Compounds*

The relatively recent findings of superconductivity in Th_4H_{15} (*1*) and PdH_x (*2–7*) has prompted us to investigate hydride formation of intermetallic compounds between Th and Pd as well as the superconducting behavior of these hydrides. The binary system Th–Pd harbors the phases (*8*) $ThPd_4$ (cubic Cu_3Au type), $ThPd_3$ (hexagonal Ni_3Ti type), Th_3Pd_5 (hexagonal Th_3Pt_5 type), ThPd (orthorhombic FeB type), and Th_2Pd (tetragonal C16 type). These materials were prepared by induction melting of the components (Th, 99.95%; Pd, 99.9%) under Ar and quenching from the melt. Where needed, the ingots were subsequently annealed at 800°C ($ThPd_4$, ThPd). The existence of crystal structures as previously reported was verified by X-ray diffraction. Hydriding of these compounds was accomplished in stainless steel containers, the amount of hydrogen take-up being monitored by pressure measurements in known volume systems (*8*). Hydriding characteristics are presented in Table I. Only Th_3Pd_5, ThPd, and Th_2Pd absorb noticeable amounts of hydrogen ($Th_3Pd_5H_{\sim 4}$, $ThPdH_4$, Th_2PdH_6) in the range from room temperature to 200°C and pressures up to 100 atm. Th_2PdH_6 and $Th_3Pd_5H_4$ are pyrophoric under air. X-ray diffraction analysis of the new hydrides proved the absence of the hydrides of Th and indicated a crystal structure different from the parent intermetallic in the case of Th_2PdH_6 and $ThPdH_4$. $Th_3Pd_5H_4$ shows a practically unchanged X-ray diffraction pattern compared with Th_3Pd_5. Further structural analyses was not attempted at this time. Superconductivity was measured with routine inductance methods and no transitions were observed in any case down to 1.8°K.

Hydriding tendencies of compounds between Th and Pd conform to a certain degree with general expectations in compounds of lanthanides or actinides with transition metals, that is, of elements with greatly different electronegativities and affinities for hydrogen (as measured in their heats of hydride formation). Hydride formation can be expected to take place at room temperature and pressures around 1 atm (given favorable kinetics) when heats of formation (ΔH) are exothermic with about −8 kcal/mole of H_2. Under these circumstances the expression for the equilibrium pressure P_e,

$$\ln P_e = \Delta H/RT - \Delta S/R,$$

yields values for P_e of about 1 atm at room temperature since the entropy term is comparable in all cases of hydrogen uptake in an intermetallic compound (of order −30 cal/mole of H_2 K). Values of ΔH, in turn, appear to lie approximately on lines connecting the values of the elements as we have shown for hydrides of Pr–Co (*8*) compounds. A similar regularity pertains to the amount of hydrogen take-up. These general trends are well reflected in the present study. The ratio of hydrogen to metal indeed increases towards Th-rich compounds and the compounds with high transition metal concentration ($ThPd_3$ and $ThPd_4$) appear to require higher H_2 pressures than available in our experiments for hydrogen take-up to be observed. Moreover, the heats of hydride formation indeed lie more or less on a straight line. If this line is extrapolated towards Pd an endothermic heat of hydride formation of +3 kcal/mole of H_2 is obtained for pure Pd. This is similar to other transition metals, such as Ni or Co. However, this value does not conform to experiment. Pd shows exothermic heats of hydride formation ranging from −3 to −11 kcal/mole of H_2 according to the amount absorbed. It appears therefore that Pd behaves similarily to other transition metals (Group 6 to Group 10 metals with the exception of Pd form hydrides endothermally) in intermetallic compounds but represents an exception in its elemental form. It should be noted that the electronegativity of Pd of 2.2 is

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* This work was supported by Grant NSG 3034 from National Aeronautics and Space Administration.

TABLE I

HYDRIDING CHARACTERISTICS OF Th–Pd COMPOUNDS

Matrix	Structure	Hydride formed	H/M	ΔH (kcal/mole of H_2)
Th	A_1 (cub.)	Th_4H_{15}	3.75	−33
		ThH_2	2.0	−35
Th_2Pd	C16 (tet.)	Th_2PdH_6[a]	2.0	
ThPd	FeB (o.rh.)	$ThPdH_4$	2.0	∼−18
Th_3Pd_5	Th_3Pt_5 (hex.)	$Th_3Pd_5H_4$[a]	0.5	∼−8
$ThPd_3$	$TiNi_3$ (hex.)	—		
$ThPd_4$	$AuCu_3$ (cub.)	—		
Pd	A_1 (cub.)	$PdH_{0.65}$	0.65	−2.8
		$PdH_{0.225}$	0.225	−11

[a] Pyrophoric under air.

slightly higher than the one of hydrogen of about 2.1 (as is the one of Pt and the rest of the noble transition metals for that matter) while the one of Ni, Co, or Fe (*1*, *8*) is somewhat lower. Therefore, one can anticipate a somewhat different charge transfer in both cases, Pd becoming more negative on hydride formation while Ni would become more positive. On this basis one could expect heats of formation versus composition to go to zero when weighted electronegativities of actinide and Pd approximate the one of hydrogen and to decrease again at higher Pd concentration. Such a saddle point picture, however, would not be commensurate with the remainder of the noble transition metals which form hydrides endothermally but rather corroborate once over the exceptional nature of Pd. The absence of superconductivity in a ternary system where metals form superconducting hydrides will hinge on various factors. Beyond an unfavourable structure one explanation would have to do with an unfavourable electron configuration. Th behaves as tri- or tetravalent metal in intermetallic compounds. Therefore, small amounts of Th compared to say Cu would have to be alloyed to Pd in order to reach a characteristic electron concentration which triggers superconductivity when the alloy is hydrided. All compounds between Th and Pd, however, are considerably beyond this electron concentration, Th, on the other hand, becomes superconducting at an unusual stoichiometry with hydrogen (Th_4H_{15}) at relatively large hydrogen concentrations. It is possible, therefore, that higher hydrogen concentrations in the intermetallic compounds in question would be beneficial for superconductivity. For this purpose synthesis of hydrides at higher pressures is in preparation in this laboratory. Synthesis at higher temperatures on the other hand is detrimental as equilibrium pressures increase with temperature in cases where hydride formation is exothermic, and, in addition, decomposition of the hydrides into hydrides of Th and elemental Pd is favored.

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Received August 12, 1975