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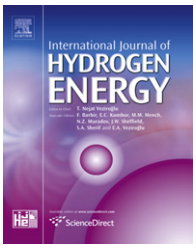

Interaction in $CeCo_{2.95}M_{0.05}$–H_2 (M-Cu, Si) system

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ABSTRACT

Interaction of hydrogen with $CeCo_{2.95}M_{0.05}$ (M-Cu, Si) intermetallic compounds has been studied under pressure of hydrogen up to 100 atm. Obtained hydrogen desorption isotherms showed a presence in the investigated systems $CeCo_{2.95}M_{0.05}$(M-Cu, Si)–H_2 several hydride phases. Introduction of Si into $CeCo_3$ alloy leads to stability decreasing of hydride phases, while introduced Cu weakly increases its stability. X-ray analysis has shown that formed in both systems hydride phases have symmetry of initial alloys with strongly increased c parameter of the lattice.

1. Introduction

Intermetallic compounds (IMS) absorb reversibly substantial amounts of hydrogen and are perspective materials for storage hydrogen in different applications. With well-studied hydrides of RT_5 and AB_2 compounds are also interesting hydrides based on RT_3 compounds with rare-earth element from cerium subgroup and T-element Ni and Co. It is known that interaction of RT_3 compounds with hydrogen leads to forming hydride phases containing about 1.5 mass. % of hydrogen [1]. For example in $CeCo_3$–H_2 system equilibrium hydrogen pressure at 75 °C is about 0.5 atm and this allows using compounds based on $CeCo_3$ for storage hydrogen. It was proposed that partially replacement of Co in $CeCo_3$ alloy would lead to changing their sorption properties and equilibrium pressure of hydride phases dissociation formed in IMC-hydrogen system.

At present work has been studied interaction of hydrogen with $CeCo_{2.95}M_{0.05}$ (M-Cu, Si) compounds under hydrogen pressure up to 100 atm.

2. Experimental

Samples of $CeCo_{2.95}Cu_{0.05}$ and $CeCo_{2.95}Si_{0.05}$ were obtained by melting in electrical furnace under inert atmosphere and after that were annealed at 950 °C during 240 h. Synthesis of hydrides and study of equilibrium in the system were carried out on the Sivert's apparatus with range of pressure up to 100 atm. During synthesis of hydrides was used "soft" method of synthesis when hydrogen was delivered consequently into reactor with small portion at pressure about 0.5 atm until to appearance of the saturated hydride. This method allows avoiding forming of amorphous hydrides. X-ray analyses of alloys and hydrides were conducted on DRON-2 diffractometer.

3. Results and discussion

X-ray analyses obtained $CeCo_{2.95}Cu_{0.05}$ and $CeCo_{2.95}Si_{0.05}$ alloys showed that the samples were single-phases and have

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Table 1 – Cell parameters of intermetallic compounds based on $CeCo_3$.

Composition	a (Å)	c (Å)	V(Å^3)
$CeCo_3$ [2]	4.933(3)	24.64(1)	519
$CeCo_{2.95}Cu_{0.05}$	4.945(2)	24.70(1)	523
$CeCo_{2.95}Si_{0.05}$	5.036(3)	25.20(2)	554

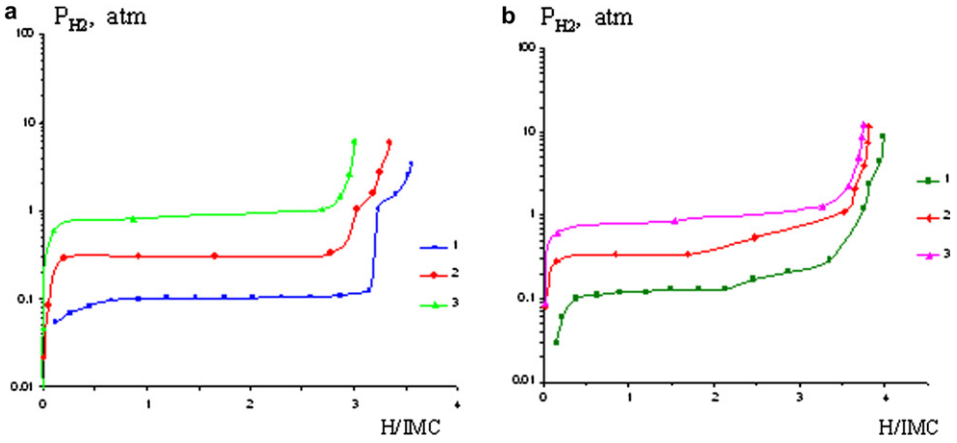

Fig. 1 – Desorption isotherms in $CeCo_{2,95}Cu_{0,05}$–H_2 (a) and $CeCo_{2,95}Si_{0,05}$–H_2 (b) systems at: 1–50 °C, 2–75 °C and 3–99 °C temperature.

hexagonal symmetry of $CeCo_3$ compound. Cell parameters are presented in Table 1. From this table it is seen that cell parameters of compound with Cu are weakly increased because of the bigger atomic radius of Cu in comparison with Co atomic radius. In alloy with Si both cell parameters are increased and cell volume rose for about 5% because of the large atomic radius of Si in comparison with Co radius.

Measured desorption isotherms of hydrogen for $CeCo_{2.95}Cu_{0.05}$–H_2 system at 50 °C, 75 °C and 99 °C (Fig. 1) revealed presence of two phases with composition close to $CeCo_{2.95}Cu_{0.05}H_3$ and $CeCo_{2.95}Cu_{0.05}H_4$, similar to $CeCo_3$–H_2 system [1]. Decreasing of the pressure equilibrium in comparison with $CeCo_3$–H_2 system shows that presence of Cu in the alloy composition leads to forming more stable phases.

Introduction of Si into $CeCo_3$ alloy composition leads to more substantial difference in behaviour of formed hydride phases. As seen from presented at Fig. 1 isotherms in $CeCo_{2.95}Si_{0.05}$–H_2 system at 50 °C it is possible to propose existence of three hydride phases: two, three and tetrahydride. With increasing of temperature desorption the slope of the isotherms is disappear and this indicates on existence of single hydride phase. Introduction of Si in the alloy composition generates opposite results in comparison with Cu and in the IMC-hydrogen system equilibrium pressure of hydrogen dissociation is increased.

Table 2 – Thermodynamic data of $CeCo_{2,95}Cu_{0,05}$–H_2, $CeCo_{2,95}Si_{0,05}$–H_2 and $CeCo_3$–H_2 systems.

System	Phase transition	ΔH, Dj/(molH_2·K)	ΔS, κDj/molH_2
$CeCo_{2.95}Cu_{0.05}$–H_2	$H_3 \leftrightarrow \alpha$	46.20	120.63
$CeCo_{2.95}Si_{0.05}$–H_2	$H_3 \leftrightarrow H_2$	34.01	94.04
	$H_2 \leftrightarrow \alpha$	30.13	110.04
$CeCo_3$–H_2 [1]	$H_3 \leftrightarrow \alpha$	38.07	135.04

Different behaviour of hydride phases based on $CeCo_3$ compounds with Cu and Si is occurred because of the influence of two factors: changing of the vacation volume in the lattice and difference chemical interactions between of the hydrogen and metallic atoms surrounding these vacations. Increased volume of vacation into lattice containing Si leads to appearance of weak metal-hydrogen bonds and hydrogen phase becomes forming under higher pressure of hydrogen. In case of Cu in the alloy composition, more important is factor of chemical interaction than factor of size vacations in the lattice.

X-ray analyses synthesized hydride phases showed that they have symmetry of initial $CeCo_3$ compound and their lattice anisotropically expanded with parameter c increased.

Thermodynamic data of hydride phases dissociation in studied systems are presented at Table 2.

Obtained results allow to make a summary, that small changing of $CeCo_3$ chemical composition influence strongly at properties of hydride phases forming in the IMC-hydrogen systems. For more detailed study of behaviour into $CeCo_{2.95}Si_{0.05}$–H_2 system it is worth to continue revise it again.

4. Conclusions

Interaction in $CeCo_{2.95}M_{0.05}$–H_2 (M-Cu, Si) systems under hydrogen pressure up to 100 atm has been studied by using pressure–composition isotherms measurements. Were

determinate the pressure of dissociation of hydride phases and their thermodynamic parameters. Introduction of Cu in alloy composition leads to increase of hydride phases stability but hydride phases with Si are less stable. X-ray analyses revealed that three hydride phases have anisotropically expanded lattice with symmetry of initial alloys.

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