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# Thermodynamic particularities of some CeNi<sub>5</sub>-based metal hydride systems with high dissociation pressure

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## Abstract

The thermodynamic behaviour of the CeNi<sub>5</sub>-H<sub>2</sub>, Ce<sub>0.8</sub>La<sub>0.2</sub>Ni<sub>5</sub>-H<sub>2</sub> and Ce<sub>0.8</sub>La<sub>0.2</sub>Ni<sub>4.7</sub>Cu<sub>0.3</sub>-H<sub>2</sub> systems during a few activation absorption-desorption cycles was studied by means of high gaseous pressure technique. *P*-*C* isotherms in the temperature range from 273 to 353 K were measured and thermodynamic parameters for hydride formation and decomposition reactions were calculated. For all studied systems the same hydrogen capacity (6.5–6.8 H atoms per AB<sub>5</sub> unit at 1000 atm and 296 K) and the same isotherm shape with a long nearly horizontal plateau and very large hysteresis were obtained. The change in alloy composition in the range CeNi<sub>5</sub> → Ce<sub>0.8</sub>La<sub>0.2</sub>Ni<sub>5</sub> → Ce<sub>0.8</sub>La<sub>0.2</sub>Ni<sub>4.7</sub>Cu<sub>0.3</sub> led to an increase in plateau length and a decrease in hysteresis factor  $P_{\text{abs}}/P_{\text{des}}$ . The hysteresis factor also decreased considerably after two or three activation cycles, by 4–8 times as compared with the first cycle. This phenomenon was connected not only with an absorption pressure decrease but also with a significant increase in desorption pressure. The relative change  $P_1/P_{\text{act}}$  in equilibrium pressure during the activation did not depend on alloy composition for the absorption reaction, but in the case of desorption it decreased with partial substitution of Ce and Ni by La and Cu correspondingly.

*Keywords:* Intermetallic hydrides; Hysteresis; High pressure

## 1. Introduction

CeNi<sub>5</sub>-based metal hydride systems take a particular place among hydride-forming intermetallic compounds. Firstly, they are characterized by a large capacity and a higher dissociation pressure that bring about a special interest in their application in heat pumps and thermosorption compressors. However, there is a very large hysteresis of hydride formation and decomposition reactions for CeNi<sub>5</sub> and its derivatives. Furthermore, a first hydriding of Ce-rich AB<sub>5</sub>-type alloys requires a much higher hydrogen pressure than equilibrium absorption hydriding after a few activation cycles [1]. These particularities caused certain problems in their experimental studies. For example, Mordkovich et al. [2] did not succeed in hydride synthesis for Ce<sub>0.7</sub>La<sub>0.3</sub>Ni<sub>5</sub> at constant temperature (373 K). Only by heating in a closed volume under hydrogen pressure (“alternate” hydriding method) was a hydride phase called “metastable” obtained. These researchers concluded that cerium content increase in solid solution Ce<sub>x</sub>La<sub>1-x</sub>Ni<sub>5</sub> led to decrease in the critical temperature value and it was close to 360 K for  $x = 0.7$ , i.e. the experimental temperature was the

supercritical temperature for this alloy composition. However, another explanation of the phenomenon may be proposed: the hydrogen pressure used was insufficient for alloy activation at constant temperature. The present work was carried out for a more detailed study of alloy composition, temperature and activation cycling effect on the thermodynamic parameters (absorption and desorption equilibrium pressures, hysteresis factor, enthalpy and entropy changes) of hydrogen interaction with CeNi<sub>5</sub> intermetallic compound and Ce<sub>0.8</sub>La<sub>0.2</sub>Ni<sub>5</sub> and Ce<sub>0.8</sub>La<sub>0.2</sub>Ni<sub>4.7</sub>Cu<sub>0.3</sub> solid solutions.

## 2. Experimental details

The samples were prepared from pure metals by arc melting under an inert atmosphere.

The high gaseous pressure technique was used to widen the pressure range of the investigation. The desorption of experimental apparatus as well as its parameters and a measurement procedure were presented in Ref. [1]. For more precise determinations of pressure-composition *P*-*C* isotherms and thermody-

namic functions of corresponding reactions the equation of state for hydrogen under high pressure [3] and calculated hydrogen fugacity values [4] were used.

### 3. Results and discussion

#### 3.1. Activation

We presented the results of the  $\text{CeNi}_5\text{-H}_2$  system investigation in our recent paper [1], where thermodynamic functions were calculated on the basis of experimental data of an activated sample. To ensure the complete reproducibility of  $P\text{-}C$  isotherms several absorption-desorption cycles were preliminarily accomplished. In the present work particular attention was paid to the behaviour of alloys during the first hydriding. A threefold repetition of this reaction for samples of the same composition at similar conditions showed that the reaction parameters were characterized by a high reproducibility, i.e. they were not determined by random factors, and so they might be applied for an analysis of activation regularities of different alloys. We would like to note only one particularity that we have determined for the studied  $\text{CeNi}_5$ -based systems and which required special attention with the similar metal-hydrogen system studies. This concerned the extremely slow kinetics of the interaction of non-activated alloys with hydrogen, which led to an exposure time increase up to several days to achieve a real equilibrium.

The hydrogen absorption and desorption isotherms for the first and the third cycles for  $\text{CeNi}_5$ ,  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5$  and  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3}$  are shown as Figs. 1, 2 and 3 respectively. The numerical values of equilibrium pressures for  $\text{AB}_5\text{H}_{3.5}$  compositions, i.e.

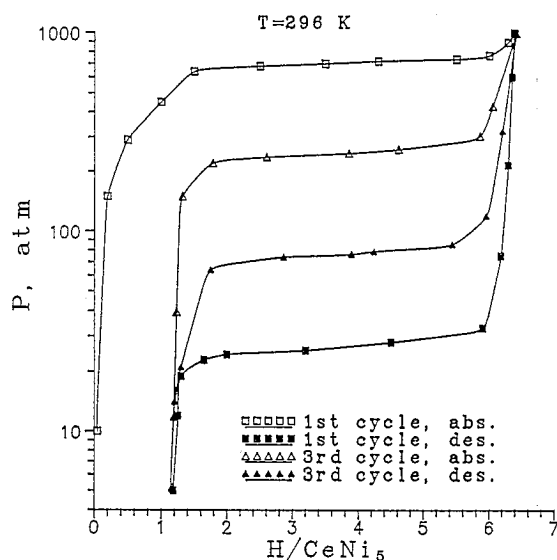


Fig. 1.  $P\text{-}C$  isotherms for  $\text{AB}_5\text{-H}_2$  systems for activation cycling:  $\text{CeNi}_5$ .

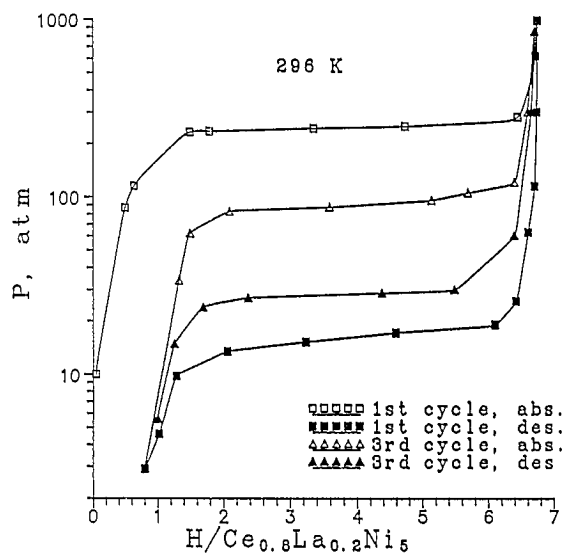


Fig. 2.  $P\text{-}C$  isotherms for  $\text{AB}_5\text{-H}_2$  systems for activation cycling:  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5$ .

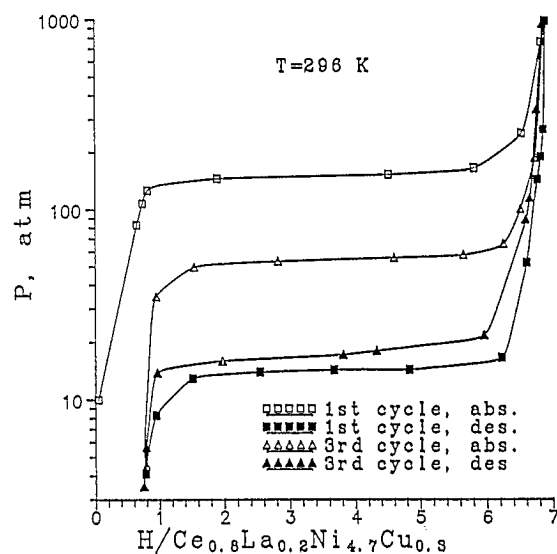


Fig. 3.  $P\text{-}C$  isotherms for  $\text{AB}_5\text{-H}_2$  systems for activation cycling:  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3}$ .

approximately a plateau mid-point, are presented in Table 1. The isotherms for the third cycle were chosen for comparison because they demonstrated no varia-

Table 1

Variations in equilibrium pressures for  $\text{CeNi}_5\text{-H}_2$ ,  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5\text{-H}_2$  and  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3}\text{-H}_2$  systems during activation at 296 K

	$\text{CeNi}_5$	$\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5$	$\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3}$
$P_{1\text{abs}}$ (atm)	698	251	151
$P_{1\text{des}}$ (atm)	25.3	16.5	14.4
$(P_{\text{abs}}/P_{\text{des}})_1$	27.6	15.2	10.5
$P_{3\text{abs}}$ (atm)	248	89.0	53.3
$P_{3\text{des}}$ (atm)	72.5	28.1	19.0
$(P_{\text{abs}}/P_{\text{des}})_3$	3.4	3.2	2.8
$(P_1/P_3)_{\text{abs}}$	2.8	2.8	2.8
$(P_3/P_1)_{\text{des}}$	2.9	1.7	1.3

tions with further cycling and could be estimated as corresponding to the activated state of the system.

Some regularities in the alloys' behaviour during activation may be noted from the presented data. For all samples the hysteresis magnitude decreased with cycling owing to the decrease in absorption pressure and the increase in desorption pressure. The hysteresis value, as represented by the ratio  $P_{\text{abs}}/P_{\text{des}}$ , changed between the first and the third cycles by factors of 8.1, 4.8 and 3.7 for  $\text{CeNi}_5$ ,  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5$  and  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3}$  respectively. Thus, the partial substitution of Ce by La and of Ni by Cu had the same effect on the  $\text{CeNi}_5\text{-H}_2$  system.

The comparison of the numerical values of pressure variations  $(P_1/P_{\text{act}})_{\text{abs}}$  and  $(P_{\text{act}}/P_1)_{\text{des}}$  with cycling for hydride formation and decomposition showed that the former value was practically independent of alloy composition and was equal to 2.8. At the same time the composition effect on the desorption pressure change was considerable:  $(P_{\text{act}}/P_1)_{\text{des}}$  decreased from 2.9 for  $\text{CeNi}_5$  to 1.7 for  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5$  and to 1.3 for  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3}$ .

It is interesting that this phenomenon was valid also for the  $\text{AB}_5$ -type intermetallic compounds which compositions were far from those studied in the present work. So according to Nomura et al. [5] for the  $\text{LaNi}_5\text{-H}_2$  system for which equilibrium pressures and hysteresis factor were significantly lower than the Ce-rich alloys, the parameter  $(P_1/P_{\text{act}})_{\text{abs}}$  was close to 2.8, coinciding with the corresponding value obtained in this work. Desorption pressure was practically independent of cycling, i.e.  $(P_{\text{act}}/P_1)_{\text{des}}$  for  $\text{LaNi}_5$  was close to 1.0.

The following explanation of the composition effect on the  $(P_{\text{act}}/P_1)_{\text{des}}$  value variations could be proposed. In the sequence  $\text{CeNi}_5 \rightarrow \text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5 \rightarrow \text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3} \rightarrow \text{LaNi}_5$  one can see a significant increase in the plateau length, corresponding to a two-phase ( $\alpha + \beta$ ) region, i.e. the difference in composition of  $\alpha$  and  $\beta$  phases in equilibrium increased. In this case  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \alpha$  transitions corresponded to maximal  $\text{LaNi}_5$  and minimal  $\text{CeNi}_5$  phase composition and lattice volume variations. The latter, in their turn, characterize the lattice strain level due to absorption-desorption cycling. According to the experimental results in Ref. [5], the lattice strain increase contributed to alloy activation acceleration. In our case it meant that the partial substitution of Ce by La and of Ni by Cu even after the first hydriding drew the system nearer to the activated state. Therefore, the first desorption parameters differed less from those for activated samples:  $(P_{\text{act}}/P_1)_{\text{des}}$  decreased.

This explanation requires, however, a supplementary experimental confirmation, notably direct X-ray and granulometric studies of hydride phases, which are very difficult because of the instability of Ce-rich

$\text{AB}_5$ -type hydrides. In all cases it is not clear which properties of this group of intermetallic compounds will condition the invariability of the  $(P_1/P_{\text{act}})_{\text{abs}}$  parameter for a wide range of compositions.

### 3.2. Thermodynamic parameters of activated state

As mentioned above, after three absorption-desorption cycles for all studied alloys we observed full reproducibility of  $P$ - $C$  isotherms. This meant that the systems became completely activated. Isotherms for three temperatures corresponding to this activated state are shown in Figs. 4, 5 and 6.

The main result of the analysis of these isotherms was that for all studied systems the critical temperature  $T_c$  value exceeded 353 K. Even at this tempera-

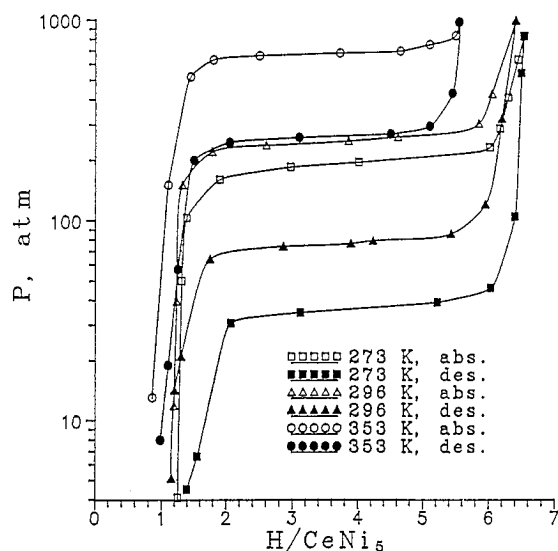


Fig. 4.  $P$ - $C$  isotherms for activated systems:  $\text{CeNi}_5$ .

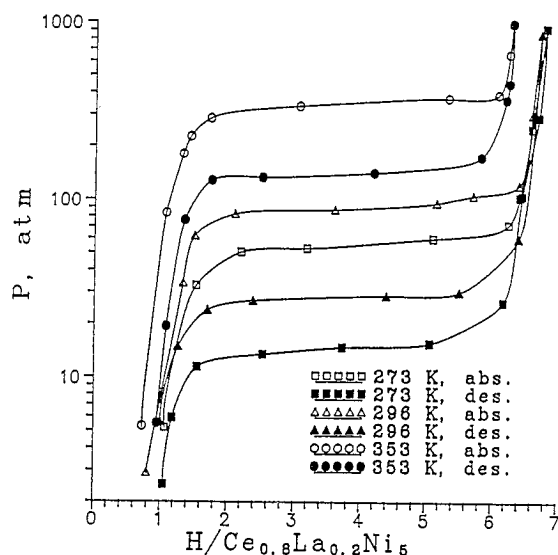


Fig. 5.  $P$ - $C$  isotherms for activated systems:  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5$ .

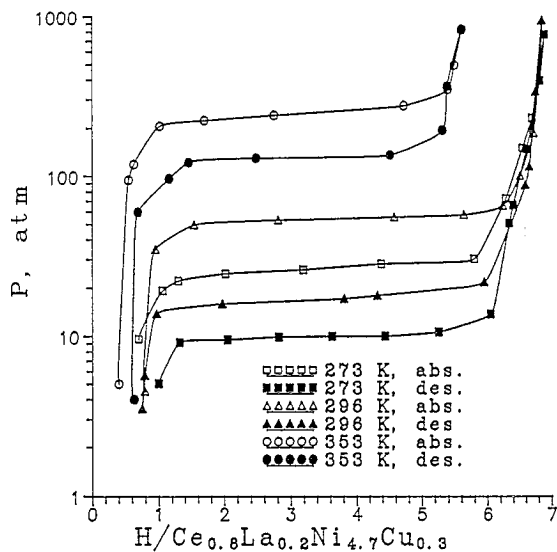


Fig. 6.  $P$ - $C$  isotherms for activated systems:  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3}$ .

ture the isotherms were characterized by the presence of an extended plateau corresponding to a two-phase equilibrium region. Available data did not permit us to determine exact  $T_c$  values. However, a qualitative estimation could be made. The plateau length variation with temperature might serve as such an estimation parameter. In fact, according to the general shape of phase diagrams for metal-hydrogen systems a significant plateau reduction with increased temperature must indicate the vicinity of the critical point. In consideration of these notes, analysis of the curves in Figs. 4, 5 and 6 might give us some information on the composition effect on the  $T_c$  value.

Firstly, lanthanum addition in  $\text{CeNi}_5$  led to a rise in  $T_c$ : the plateau length reduction with the temperature increase from 273 to 353 K was smaller for La-substituted alloys (see Figs. 4 and 5). The same conclusion was drawn in Ref. [2] for the  $\text{La}_{1-x}\text{Ce}_x\text{Ni}_5$  alloys, although the quantitative estimation of  $T_c$  values made by the authors of this work (for example, 360 K for  $\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_5$ ) seemed not to be correct. According to our data  $T_c$  for this composition must be considerably higher.

Secondly, partial substitution of Ni by Cu had an opposite effect although all room temperature measurements during activation indicated that there ex-

isted a similarity of thermodynamic variations with the additions of Cu and La. However, at the elevated temperature the two-phase region of  $P$ - $C$  isotherms for the  $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3}$ - $\text{H}_2$  system was significantly reduced (Fig. 6). This system was thus characterized by an unusual combination of higher thermal stability and lower  $T_c$  value in comparison with  $\text{CeNi}_5$ .

The temperature effect on the hysteresis magnitude was considerable and the effects were similar for all studied alloys. With temperature increase the ratio  $P_{\text{abs}}/P_{\text{des}}$  decreased as for most metal-hydrogen systems. The hysteresis magnitude variation caused by temperature change was weakly dependent on alloy compositions and was close to 35%–45% for the temperature interval from 273 to 353 K.

For the thermodynamic functions  $\Delta H$  and  $\Delta S$  (calculated values are presented in Table 2) no anomalies were noted. Absorption-desorption equilibrium pressures decreased in the sequence  $\text{CeNi}_5 \rightarrow \text{CeNi}_5 \rightarrow \text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5 \rightarrow \text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3}$ ;  $\Delta H$  values increased regularly. For all systems a difference between  $\Delta H_{\text{abs}}$  and  $\Delta H_{\text{des}}$  was obtained owing to the large hysteresis. This difference characterizing the energy loss in a completing hysteresis loop decreased with La and Cu additions which correlated with the reduction in hysteresis magnitude.

The dependence of  $\Delta S$  values on composition had the same character; however, variations in this thermodynamic function were considerably smaller and did not exceed 2%–3%.

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Table 2  
Thermodynamic parameters for activated samples

	$\text{CeNi}_5$	$\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5$	$\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.7}\text{Cu}_{0.3}$
$\Delta H_{\text{des}}$ ( $\text{kJ} (\text{mol H}_2)^{-1}$ )	$22.2 \pm 0.1$	$23.8 \pm 0.3$	$24.8 \pm 0.6$
$-\Delta H_{\text{abs}}$ ( $\text{kJ} (\text{mol H}_2)^{-1}$ )	$17.0 \pm 0.6$	$18.9 \pm 0.6$	$21.0 \pm 0.3$
$\Delta S_{\text{des}}$ ( $\text{J K}^{-1} (\text{mol H}_2)^{-1}$ )	$111.0 \pm 0.2$	$108.8 \pm 0.2$	$108.4 \pm 0.5$
$-\Delta S_{\text{abs}}$ ( $\text{J K}^{-1} (\text{mol H}_2)^{-1}$ )	$105.8 \pm 0.7$	$101.7 \pm 0.4$	$101.2 \pm 0.2$