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# Stabilisation of high dissociation pressure hydrides of formula $La_{1-x}Ce_xNi_5$ ($x$=0–0.3) with carbon monoxide

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## Abstract

We have previously demonstrated the efficiency of CO and $SO_2$ surface treatments for the stabilization of the $LaNi_5$ hydride. The as-treated hydrides were stable in air at room temperature. Here, CO surface treatment is applied to higher dissociation pressure systems, $La_{1-x}Ce_xNi_5$ ($x$=0, 0.1, 0.2 and 0.3) compounds. Stabilization of the hydrides is studied at two temperatures, 273 and 298 K. We found that the hydrogen retention time for CO-treated $La_{1-x}Ce_xNi_5$ hydrides is dramatically improved compared with that of untreated hydrides. Nevertheless, for both temperatures, the hydrogen retention time in treated hydrides is found to decrease with increasing cerium content. The results are explained on the basis of $P$–$C$–$T$ measurements carried out at room temperature. As expected, the hydrogen absorption and desorption pressures and the hysteresis increase with cerium content. The dehydrogenation kinetics of CO-treated hydrides is related to the cerium content of the alloys. © 1998 Elsevier Science S.A.

*Keywords:* Carbon monoxide; Cerium substitution; Hydrogen storage; $LaNi_5$; Poisoning

## 1. Introduction

$CeNi_5$-type alloys have been studied by many authors since they absorb a large quantity of hydrogen and their hydrides are characterized by a high dissociation pressure which attracts special interest for their application in heat pumps and thermosorption compressors. Cerium is also one of the main components of mischmetal (from 10% in lanthanum-rich mischmetal [1] to 50% in mischmetal), which is now used in $MmNi_5$-type batteries.

The hydriding characteristics of the $CeNi_5$–$H_2$ system were found to be low kinetics of hydride formation and decomposition, very high equilibrium pressure (7.25 MPa at 296 K), large hydrogen content (6.0 hydrogen atoms per $CeNi_5$ formula at 295 K), and a large hysteresis value ($\ln(P_{abs}/P_{des}) = 1.23$ at 296 K) [2]. $La_{1-x}Ce_xNi_5$ compounds have been studied by Uchida and co-workers [3]. They reported that the addition of cerium produced a significant hysteresis effect and a large increase in both the absorption and desorption pressures, whereas the total amount of hydrogen absorbed by the hydride was less affected. Some cerium-based compounds also exhibit different cerium valence states, which could affect the intrinsic properties of the alloys and hydrides. Takeshita and co-workers studied $CeNi_4Al$ hydriding properties and found that the effective valence of cerium in $CeNi_4AlH_{3.7}$ was between 3 and 4, according to lattice volume calculations [4]. Pasturel et al. studied $Ce(Ni_{1-x}Cu_x)_5$ compounds and found a cerium valence greater than 3 from the determination of the enthalpies of formation ($\Delta H_f$) [5]. They found that the value of $\Delta H_f^{298}$ is $-199$ kJ mol$^{-1}$ for $CeNi_5$, which is much lower than the $-159$ kJ mol$^{-1}$ for $LaNi_5$. Recent values of $\Delta H_f^{298}$ are given by Yamaguchi et al. [6]; they found a $\Delta H_f^{298}$ value of $-136$ kJ mol$^{-1}$ for $LaNi_5$ and $-166$ kJ mol$^{-1}$ for $CeNi_5$, thanks to a different method of enthalpy measurement. Colinet and Pasturel estimated a value of $-39$ kJ mol$^{-1}$ for the energetic effect associated with the valence change of Ce in $CeNi_5$ [7]. A XANES study of $CeNi_5$ demonstrated the coexistence of $Ce^{3+}$ and $Ce^{4+}$ states in the compound [8].

Also, it is well known that impurities found in hydrogen gas such as carbon monoxide and other sulfur compounds have the effect of poisoning the alloy surface, and consequently reducing the hydrogen uptake [9–11]. As reported

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in our previous papers [12–14], carbon monoxide and sulfur dioxide were used as a surface poison of $LaNi_5H_6$ hydride in order to confine hydrogen. For example, after 300 ks of air exposure at 298 K, more than four hydrogen atoms per $LaNi_5$ formula remained in the CO-treated hydride, whereas the untreated hydride was completely dehydrogenated in 40 ks.

In the present study, we investigate the efficiency of CO treatment on higher dissociation pressure hydrides, such as $La_{1-x}Ce_xNi_5$ ($x=0$, 0.1, 0.2 and 0.3). The stabilization of the hydrides was studied at different temperatures, in air, at atmospheric pressure. Pressure–composition–temperature measurements permitted us to determine the absorption and desorption pressures as a function of the cerium content, which was also related to the dehydrogenation kinetics of the CO-treated hydrides.

## 2. Experimental

### 2.1. Powder preparation

$LaNi_5$ ingots were supplied by Santoku Metal Industry Co., Kobe, Japan. The synthesis method was arc-melting. $La_{1-x}Ce_xNi_5$ ($x=0.1$, 0.2 and 0.3) alloys were prepared at the Laboratoire de Cristallographie, C.N.R.S., Grenoble, France, by induction melting in a copper cold crucible under argon atmosphere.

Samples were crushed into fine powder under argon atmosphere, introduced into a quartz crystal tube and placed in the hydrogenation setup. Activation was carried out at different hydrogen pressures (1.0 MPa for $LaNi_5$ and $La_{0.9}Ce_{0.1}Ni_5$, 1.5 MPa for $La_{0.8}Ce_{0.2}Ni_5$ and 4.0 MPa for $La_{0.7}Ce_{0.3}Ni_5$) at cycling temperatures from 273 to 373 K. The purity of the hydrogen gas was 99.9995%.

### 2.2. CO surface treatment

After activation, the sample was first cooled to 77 K during 1.2 ks to keep the β-phase stable during the absence of hydrogen. The hydrogen atmosphere was then quickly removed, and 0.9 MPa of carbon monoxide (purity 99.9%) was introduced into the sample holder for 300 s, according to a method published elsewhere [12–14]. After this treatment, the hydride was stable in air at atmospheric pressure. The same batch of powder was then divided into two samples, one maintained at 273 K and the other at 298 K, to test the influence of temperature on hydride conservation.

### 2.3. Kinetic measurements

Kinetic measurements were performed at 298 K, with 1 g of $LaNi_5$ or $La_{0.9}Ce_{0.1}Ni_5$ powder, in order to determine the influence of cerium substitution on hydriding kinetics. The hydrogen setup was then connected to a $196\ cm^3$ hydrogen tank in order to increase the total volume of hydrogen. The ratio of the plateau pressure of the sample to the applied pressure in the system was 3 ($P_{syst}/P_{abs}=3$). The thermodynamic driving forces were then the same for the two samples, in agreement with the work of Goudy and co-workers [15,16]. The applied pressures for the hydriding kinetic measurements were 0.78 and 0.96 MPa, respectively, for $LaNi_5$ and $La_{0.9}Ce_{0.1}Ni_5$.

### 2.4. Sample characterization

X-ray diffraction (XRD) measurements were performed systematically in air, at room temperature and at atmospheric pressure, with Cu Kα radiation on a MAC Science M18XHFSRA diffractometer to control periodically the remaining amount of sealed hydrogen. The amount in the $LaNi_5$ hydrides was calculated according to the relationship between the hydrogen concentration in the samples ($H/LaNi_5$) and the ratios of peak intensities (the (111) peaks of the $LaNi_5H_{6.2}$ and $LaNi_5$ phases) published previously [12]. This relationship was re-calculated for the cerium compounds according to their $P–C–T$ diagrams. Scanning electron microscopy (SEM) was used to evaluate the average size of the particles and to observe the eventual difference in powder particle shape or surface smoothness. Electron probe micro-analysis (EPMA) was used to determine the accurate composition of the bulk alloys. The carbon content of the powders was determined with a HORIBA EMIA-810-type apparatus for the raw materials and the CO-treated hydrides. Pressure–composition–temperature measurements were realised on activated samples at room temperature, under a hydrogen pressure of up to 5.0 MPa. The purity of the hydrogen gas used was 99.99999% for this experiment.

## 3. Results and discussion

SEM observations of CO-treated $La_{1-x}Ce_xNi_5$ established that the average particle size of all samples was 20 μm after the activation procedure under hydrogen. The powder grains exhibited some cracks due to the activation with hydrogen, and all appeared identical disregarding the cerium content. The cerium concentration in the $La_{1-x}Ce_xNi_5$ samples was determined by EPMA, and the results are presented in Table 1, together with the lattice parameters and cell volume of the samples calculated with the CELREF refinement program [17]. Information regarding $CeNi_5$ from the work of Meyer–Liautaud is also shown [5]. The structure of all the samples was refined in the $P6/mmm$ space group. We observed a strong decrease of both lattice parameter $a$ and the cell volume with cerium concentration. Concurrently, lattice parameter $c$ increased slightly with cerium content. It is well known that the cell volume of $RENi_5$ compounds decreases along

Table 1
Cerium content of $La_{1-x}Ce_xNi_5$ samples ($0 \leq x \leq 1$) from electron probe micro-analysis together with the lattice parameters and cell volume of the samples from CELREF refinement program calculations. The change of lattice volume versus that of the $LaNi_5$-type is also reported

| Sample | Cerium concentration (%) | Lattice parameter (nm) | | Cell volume $V$ (nm$^3$) | $\Delta V/V$(%) | Ref. |
|---|---|---|---|---|---|---|
| | | $a$ | $c$ | | | |
| $LaNi_5$ | 0 | 0.5020(1) | 0.3988(1) | 0.08703 | Reference | This work |
| $La_{0.9}Ce_{0.1}Ni_5$ | 12 | 0.5002(1) | 0.3993(1) | 0.08652 | −0.58 | This work |
| $La_{0.8}Ce_{0.2}Ni_5$ | 19 | 0.4983(3) | 0.3998(3) | 0.08600 | −1.18 | This work |
| $La_{0.7}Ce_{0.3}Ni_5$ | 30 | 0.4964(2) | 0.4004(1) | 0.08545 | −1.81 | This work |
| $CeNi_5$ | 100 | 0.4882 | 0.4004 | 0.08264 | −5.04 | [5] |

the lanthanide series. Only $CeNi_5$ exhibits an anomalously small lattice volume. Compared to the $LaNi_5$ cell volume, $CeNi_5$ exhibits a 5.0% lattice volume decrease, whereas the lattice volumes of $PrNi_5$ and $SmNi_5$ decreased, respectively, 2.3 and 3.9% [18]. The volume contraction due to the presence of cerium appeared to be linear for $La_{1-x}Ce_xNi_5$ with increasing cerium concentration $x$, as shown in Fig. 1. This behaviour can be understood from the valence change of cerium in $RENi_5$ compounds [5]: due to charge transfer from the 5d electron of cerium to the nickel 3d band, the Fermi energy level $E_F$ of $RENi_5$ is lower than that of RE. If the $4f^1$ level of Ce is higher than the $E_F$ of $CeNi_5$, the 4f electrons of Ce do not participate in the bonding in $CeNi_5$, and the valence state of Ce becomes greater than 3. Consequently, the cerium radius decreases significantly and an anomalously small lattice parameter $a$ and cell volume are observed for cerium-containing $RENi_5$ compounds. The lattice parameter $c$ of $RENi_5$ compounds was less affected by the cerium radius change ($r_{Ce}$), since it depends essentially of the atomic radius of Ni ($r_{Ni}$).

Kinetic measurements on $LaNi_5$ and $La_{0.9}Ce_{0.1}Ni_5$ powders were performed at 298 K in order to determine the influence of cerium substitution on the hydriding kinetics. The time for 90% hydriding versus the hydriding/dehydriding cycle number is shown in Fig. 2 for the two samples. One can observe that both samples were successfully activated after 10 hydriding/dehydriding cycles. Ninety percent of the absorption reaction was then completed in 120 s for the cerium-free compound, whereas it took more than 500 s for the $La_{0.9}Ce_{0.1}Ni_5$ sample. Thus cerium substitution appears to have a negative effect on the hydriding kinetic properties. This is in good agreement with the literature, since Klyamkin and Verbetsky studied $CeNi_5$ [2] and $La_{0.2}Ce_{0.8}Ni_5$ [19] and reported a low reaction rate and a very long equilibrium time for these two compounds. Nevertheless, Goudy and co-workers performed kinetic measurements on $MmNi_5$ (Mm = mischmetal) [16] and found that $MmNi_5$ has faster kinetics than $LaNi_5$. They quickly concluded that the presence of other rare earth elements such as cerium, praseodymium and neodymium in $MmNi_5$ produced a positive effect on the reaction kinetics. It appears here that this positive effect could come from Nd or Pr, or from the mixture of the three rare earth metals, but did not come from cerium alone.

Pressure–composition–temperature diagrams realized at 298 K for $LaNi_5$, $La_{0.9}Ce_{0.1}Ni_5$, $La_{0.8}Ce_{0.2}Ni_5$ and $La_{0.7}Ce_{0.3}Ni_5$ are presented in Fig. 3. It appears that cerium substitution did not induce a significant decrease in the hydrogen capacity of the alloys. This is in good agreement with the work of Klyamkin et al., since $CeNi_5$

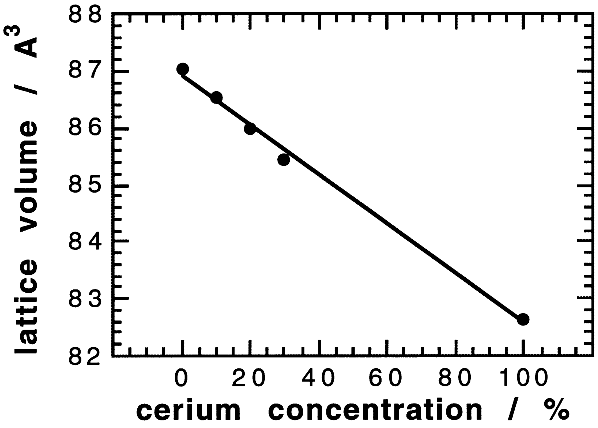

Fig. 1. Cell volume of the $La_{1-x}Ce_xNi_5$ samples versus the cerium concentration $x$.

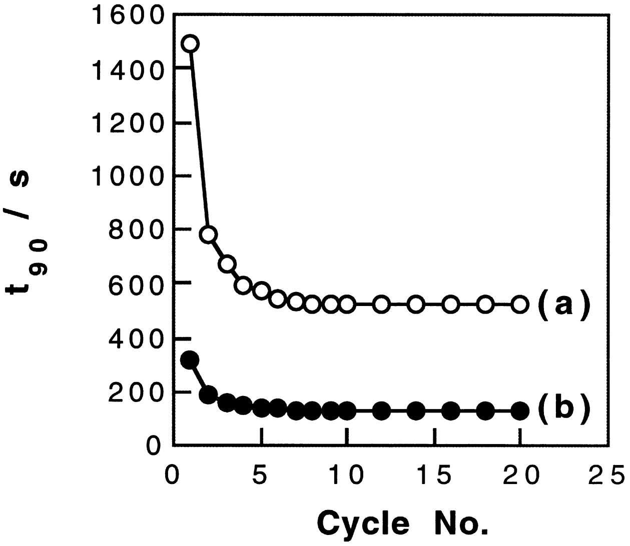

Fig. 2. Time for 90% hydriding reaction versus the cycle number for $La_{0.9}Ce_{0.1}Ni_5$ (○) and $LaNi_5$ (●).

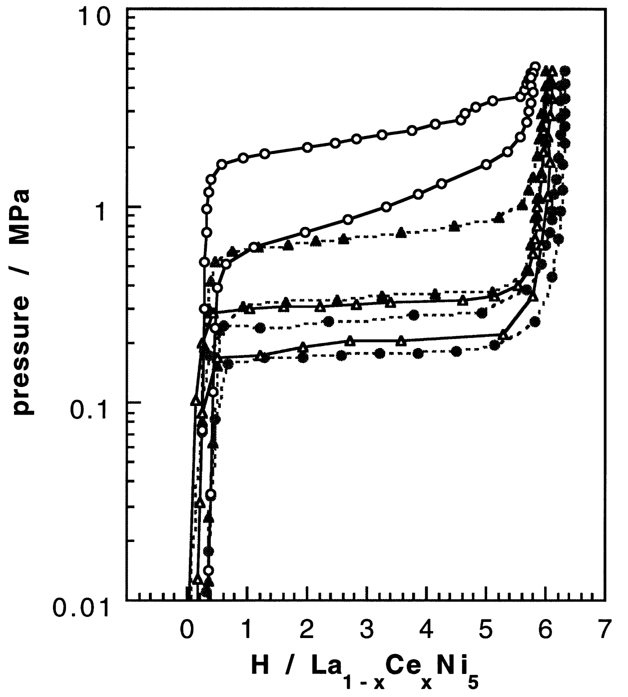

Fig. 3. Pressure–composition–temperature hysteresis recorded at 298 K for $LaNi_5$ (●), $La_{0.9}Ce_{0.1}Ni_5$ (△), $La_{0.8}Ce_{0.2}Ni_5$ (▲) and $La_{0.7}Ce_{0.3}Ni_5$ (○).

hydride exhibits the formula $CeNi_5H_6$ [2]. $La_{0.7}Ce_{0.3}Ni_5$ exhibited a hydrogen content of 5.8 hydrogen atoms per alloy formula, whereas the value was 6.2 hydrogen atoms per alloy formula for $LaNi_5$. The increase of the absorption and desorption plateau pressure versus the cerium concentration is plotted in Fig. 4. One can observe that the increase is larger for the absorption than for the desorption pressure. This is also in good agreement with the literature, since Uchida et al. reported a strong hysteresis effect in the $La_{1-x}Ce_xNi_5$–H system for $x$ values of 0.15, 0.3, 0.4, 0.5 and 0.65 [3]. They indicated an equilibrium pressure of 0.8 MPa for $La_{0.7}Ce_{0.3}Ni_5$, whereas we found 1.0 MPa here. The plateaus remained almost flat, with the exception of that for $La_{0.7}Ce_{0.3}Ni_5$, which presented a steep slope; the hysteresis factor became twice as high as for the parent compound $LaNi_5$. This was certainly due to the very slow reaction kinetics of the sample with hydrogen, and the difficulties consequently encountered during the activation procedure (the reaction kinetics become slower and slower when the reaction approaches the equilibrium state). Fig. 5 presents the plateau pressure slope of the cerium-substituted samples for both absorption and the desorption. The slope increases with cerium concentration and is higher for the absorption pressure than for the desorption pressure. The desorption pressure slope remained almost constant up to 20% cerium substitution, at a value lower than 5% per H/$LaNi_5$. We believe that the values for $La_{0.7}Ce_{0.3}Ni_5$ can be reduced with a better activation procedure.

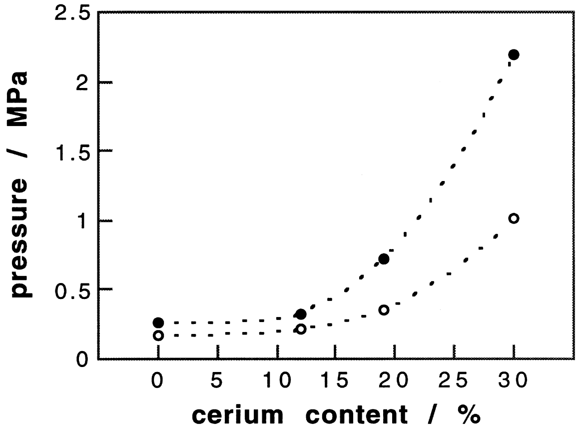

Fig. 4. Absorption plateau pressure (●) and desorption plateau pressure (○) for $La_{1-x}Ce_xNi_5$ samples versus the cerium concentration $x$.

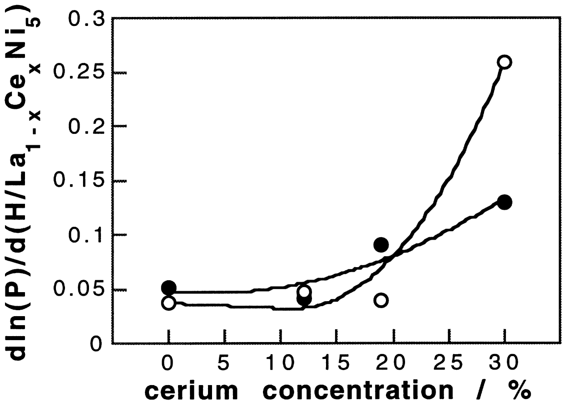

Fig. 5. Absorption plateau slope (●) and desorption plateau slope (○) for $La_{1-x}Ce_xNi_5$ samples versus the cerium concentration $x$.

The free energy loss of the $La_{1-x}Ce_xNi_5$ samples ($1/2RT\ln(P_a/P_d)$), where $P_a$ is the absorption pressure and $P_d$ the desorption pressure) due to the hysteresis effect is shown in Fig. 6 for H/M = 0.5. The free energy loss value

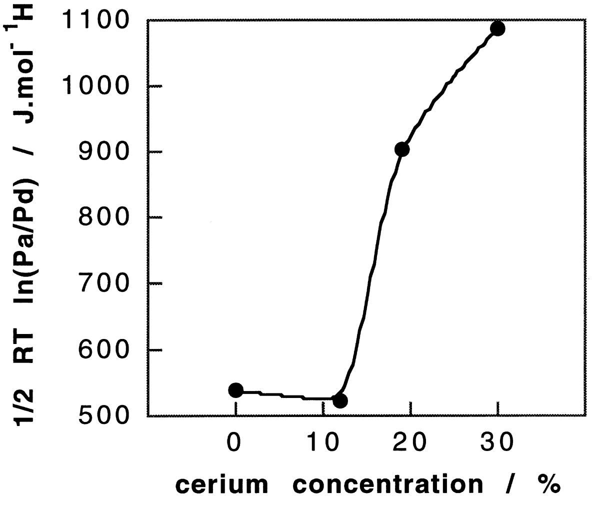

Fig. 6. Free energy loss due to the hysteresis effect for $La_{1-x}Ce_xNi_5$ samples versus the cerium concentration $x$, calculated at 298 K for H/M = 0.5.

of $LaNi_5$ is 538 J mol$^{-1}$ H, which is very close to that of $La_{0.9}Ce_{0.1}Ni_5$. The free energy loss values for higher cerium contents increase dramatically, reaching 1085 J mol$^{-1}$ H for $La_{0.7}Ce_{0.3}Ni_5$. This behaviour cannot be related to the decrease in the cell volume, since its variation with cerium content was linear.

We previously calculated the relationship between the average hydrogen content of the $LaNi_5$ hydrides and the ratio of XRD peak intensities ($LaNi_5H_{6.2}/LaNi_5$) [12]. When plotting the hydrogen concentration in $LaNi_5H_x$ versus the percentage of the β-phase ($LaNi_5H_{6.2}$), we found a linear dependence in the range 25–90%. Regarding this linear dependence and according to the slight decrease in the maximum hydrogen content of $La_{1-x}Ce_xNi_5$ hydrides compared with that of $LaNi_5$ (from the $P$–$C$–$T$ hysteresis), we re-calculated this relationship for the cerium-containing hydrides. These relationships served in the determination of the hydrogen content versus time for the CO-treated samples.

Fig. 7 shows the hydrogen concentration in CO-treated $La_{1-x}Ce_xNi_5$ hydrides versus time, at 298 K, in air, for different cerium contents. Four hydrogen atoms per $LaNi_5$ formula remained in the CO-treated $LaNi_5$ hydride after 226 ks, as previously reported [12], whereas this time was only 15 ks for the CO-treated $La_{0.9}Ce_{0.1}Ni_5$ hydride and 3 ks for the CO-treated $La_{0.8}Ce_{0.2}Ni_5$. Nevertheless, we found that CO surface treatment increased the retention time of hydrogen in the hydrides, including those containing cerium. At 298 K, the untreated $LaNi_5$ hydride was completely dehydrogenated in 32 ks, the $La_{0.9}Ce_{0.1}Ni_5$ hydride in 1.8 ks, and the $La_{0.8}Ce_{0.2}Ni_5$ and the $La_{0.7}Ce_{0.3}Ni_5$ hydrides in less than 0.6 ks.

Fig. 8 shows the hydrogen concentration in CO-treated $La_{1-x}Ce_xNi_5$ hydrides versus time, at 273 K, in air, for different cerium contents. The strong dependence of hydrogen retention on cerium concentration is confirmed. Four hydrogen atoms per $La_{1-x}Ce_xNi_5$ formula remained in the CO-treated $LaNi_5$ hydride after 820 ks, as previously reported [14], whereas this time was only 75 ks for the CO-treated $La_{0.9}Ce_{0.1}Ni_5$ hydride and 7 ks for the CO-treated $La_{0.8}Ce_{0.2}Ni_5$, showing that the CO surface treatment was enhanced by a lower temperature. The temperature effect was clearly demonstrated in our previous work [14], and is applied here to observe the dehydrogenation procedure of the CO-treated hydrides during a longer time than at 298 K. It is important to note that the lower temperature also slightly enhances the hydrogen retention time of the untreated samples, but the improvement was less important than for the CO-treated samples. The CO molecules chemisorb associatively and bond with the nickel atoms present at the hydride surface. The surface of the CO-treated hydrides was certainly not completely covered by CO molecules, leaving free pathways for hydrogen desorption. The CO coverage rate on $LaNi_5$-type samples is currently under study. Thus the higher the equilibrium pressure of the hydride, the faster the dehydrogenation kinetics, as shown in Fig. 9.

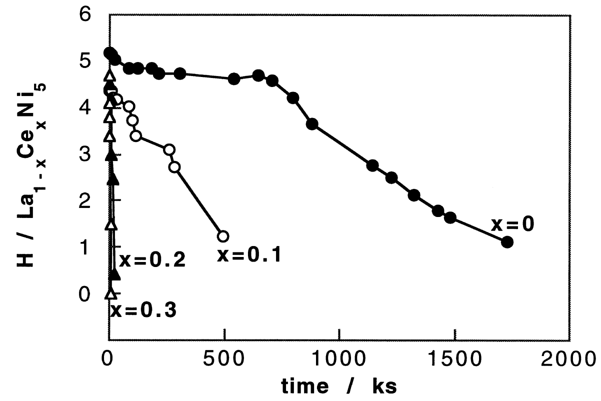

Fig. 8. Retention time of hydrogen in CO-treated $La_{1-x}Ce_xNi_5$ at 298 K in air for $0 \leq x \leq 0.3$.

On the other hand, $CeO_2$ is well known to be a good catalyst of carbon monoxide at relatively high temperature, i.e. around 500 K. We believe that the surface of the $La_{1-x}Ce_xNi_5$ samples is partially covered by cerium oxides, since rare earth metals have a strong affinity for

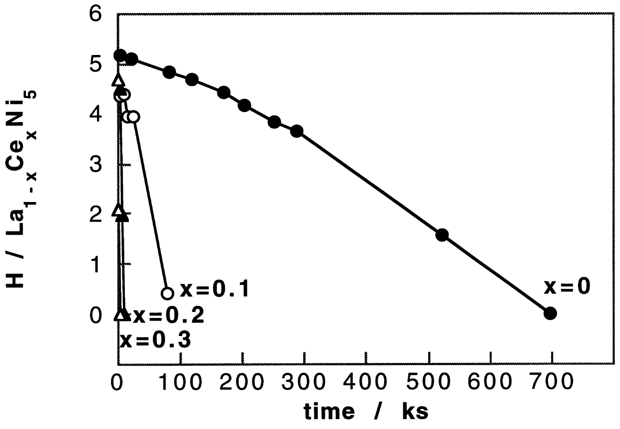

Fig. 7. Retention time of hydrogen in CO-treated $La_{1-x}Ce_xNi_5$ at 273 K in air for $0 \leq x \leq 0.3$.

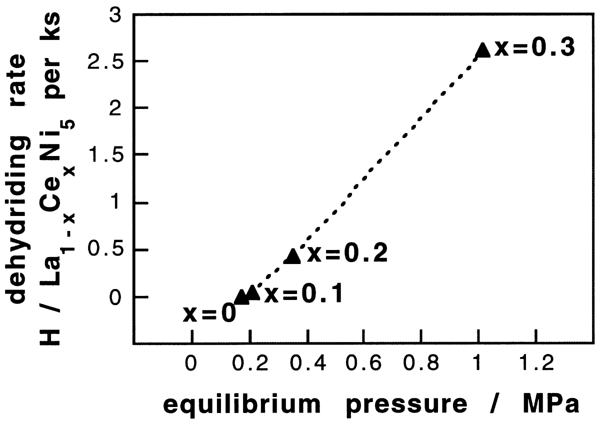

Fig. 9. Dehydriding rate of CO-treated $La_{1-x}Ce_xNi_5$ hydrides at 298 K in air versus their equilibrium pressure for $0 \leq x \leq 0.3$.

Table 2
Carbon content (ppm) from HORIBA analysis for the raw materials and the CO-treated samples

| | $LaNi_5$ | $La_{0.9}Ce_{0.1}Ni_5$ | $La_{0.8}Ce_{0.2}Ni_5$ | $La_{0.7}Ce_{0.3}Ni_5$ |
|---|---|---|---|---|
| Raw material | 230±10 | 242±15 | 113±15 | 156±10 |
| CO-treated sample | 370±10 | 472±10 | 448±13 | 444±15 |

oxygen. It is important to check the dependence of the chemisorption of the CO molecules on the CO-treated hydride surface on the cerium content of the alloys. Table 2 presents the carbon content of $LaNi_5$, $La_{0.9}Ce_{0.1}Ni_5$, $La_{0.8}Ce_{0.2}Ni_5$ and $La_{0.7}Ce_{0.3}Ni_5$ as raw materials (as-prepared bulk materials) and CO-treated samples. The four samples exhibit an average carbon content of 180 ppm as raw materials. CO surface treatment induces a large increase of the carbon content for all samples, which reached a value of 444 ppm for the CO-treated $La_{0.7}Ce_{0.3}Ni_5$ sample. These results show that the presence of cerium in the compound does not induce desorption of the CO molecules. The effect of cerium substitution on the dehydriding kinetics of CO-treated hydrides is believed to be due only to the higher equilibrium pressure.

## 4. Conclusions

This work permits us to extend the available information regarding $La_{1-x}Ce_xNi_5$ compounds (with $0 \leq x \leq 0.3$) and CO surface treatment.

- The structure of $La_{1-x}Ce_xNi_5$ samples was refined in the *P6/mmm* space group and we found that an increase in cerium content induces an important decrease in both the *a* cell parameter and the lattice volume, whereas lattice parameter *c* was less affected. This can be explained by consideration of the valence state of cerium, which remains higher than 3 in $RENi_5$ compounds.
- Hydriding kinetics at 298 K are revealed to be lower for cerium-containing compounds, in good agreement with the literature on higher cerium content compounds.
- Pressure–composition–temperature diagrams show that the absorption and desorption pressures and the hysteresis increased with cerium content. The pressure plateau slope is also found to increase, but can certainly be reduced with a better activation procedure.
- CO surface treatment extends the retention time of hydrogen in $La_{1-x}Ce_xNi_5$ hydrides, when kept in air at atmospheric pressure, and for a temperature of 273 or 298 K. Nevertheless, cerium substitution has a dramatic influence on hydrogen retention, since the time for complete dehydrogenation is 820 ks for CO-treated $LaNi_5$ hydride and only 110 ks for $La_{0.9}Ce_{0.1}Ni_5$ at 298 K. The positive effect of a lower temperature on hydrogen retention is confirmed.
- The carbon content analysis revealed that the CO molecules chemisorb in equal quantity on the $LaNi_5$ surface and on the cerium-containing compound. This indicates that the increase in dehydrogenation kinetics of CO-treated $La_{1-x}Ce_xNi_5$ hydrides with cerium content is only due to the increase of the equilibrium pressure.

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