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Structure and hydrogen storage performance of $LaNi_{4.25}Al_{0.75}$ alloy

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Abstract: Hydrogen storage properties of $LaN_{4.25}Al_{0.75}$ alloy were experimentally investigated by XRD, PC isotherm curves, hydrogen absorption kinetics curves, XPS and its particle diameter. The structure of unit cell of $LaNi_{4.25}Al_{0.75}$ alloy was deduced. The relationship between its structure and hydrogen storage performance of $LaNi_{4.25}Al_{0.75}$ alloy was analyzed. The results show that $LaNi_{4.25}Al_{0.75}$ alloy has rapid hydrogen absorption rate and good resistance to combustibility. It is also found that the function of the hydrogen absorption plateau pressure and temperature is $\ln p_{eq}=-4\ 820/T+12.46$, and the hydrogen absorption rate of the alloy decreases with increasing the temperature.

Key words: hydrogen storage alloy; $LaNi_{4.25}Al_{0.75}$; microstructure; resistance to combustibility

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1 Introduction

Hydrogen storage alloys have been widely studied for their application as energy storage media and battery electrodes[1−3]. Among these materials, $LaNi_5$ alloy exhibits excellent hydrogen storage characteristics, such as high volumetric storage density, easy activation and moderate kinetics[2]. However, $LaNi_5$ alloy has unsatisfactory properties, such as easy decay of storage capacity in cyclic absorption/ desorption process, easy pulverization, easy combustion after pulverization and higher plateau pressures [3].

It was found that the partial replacement of Ni in $LaNi_5$ alloy by a small amount of Al could prominently increase its cycle life time, pulverization and modulate moderate plateau pressures without obvious decrease in hydrogen absorption capacity[1, 4−6], so $LaNi_xAl_{5-x}$ is considered to be very useful hydrogen absorption material for its moderate plateau pressure and resistance to impurities in hydrogen gas[1, 3−5]. For example, $LaNi_{4.25}Al_{0.75}$-tritide is used in the Savannah River Site (SRS) tritium processing to be the primary tritium storage medium because the material is easily activated, a delivery pressure of 200 kPa is easily achieved by moderate heating and it captures nearly the entire tritium[7]. So, much attention has been particularly focused on $LaNi_{4.25}Al_{0.75}$ compounds for their application in energy storage[1, 7]. However, there is less report available on the relationships between structure and hydrogen storage behavior of the $LaNi_{4.25}Al_{0.75}$ alloy.

In the present work, hydrogen storage properties of $LaNi_{4.25}Al_{0.75}$ alloy were systematically studied, the structure of four-unit cell of $LaNi_{4.25}Al_{0.75}$ alloy was deduced, and the relationship between structure and its hydrogen storage performance was analyzed.

2 Experimental

Stoichiometric $LaNi_{4.25}Al_{0.75}$ alloy was prepared in a high-frequency induction melting furnace using argon atmosphere protection (lanthanum 99.50%; nickel 99.95%; aluminum 99.70%, mass fraction). Those ingots were turned over and re-melt twice for homogeneity. Those ingots were then annealed at 1 323 K for 8 h in argon atmosphere in a sealed quartz tube. About 1 g single phase $LaNi_{4.25}Al_{0.75}$ with $CaCu_5$-type hexagonal structure was individually placed in cells made of stainless steel to test hydrogen storage behavior.

The sample cell whose volume was precisely

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calibrated was then connected with testing apparatus which was set up with actuator-driven valves and needle valves. High-pressure transducers, vacuum transducers and thermocouple were attached to the system for pressure and temperature measurements. Oil bath and water bath were employed to keep temperature constant.

High-purity hydrogen (H_2≥99.999%, mass fraction) was used to test activation and PC isotherms for absorption hydrogen as well as absorption kinetics curves.

The phase composition was identified by XRD (Rigaku, Japan). The size distribution of the particles after 25 hydrogen absorption/ desorption cycles was investigated with a Malvern mastersizer mirco laser particle sizer. Surface survey of sample was carried out on LAS-3000 surface analysis systems.

3 Results and discussion

3.1 Crystal structure of $LaNi_{4.25}Al_{0.75}$ alloy

Fig. 1 shows XRD pattern of $LaNi_{4.25}Al_{0.75}$ alloy annealed, and the alloy is identified as single phase material with the $CaCu_5$-type hexagonal structure.

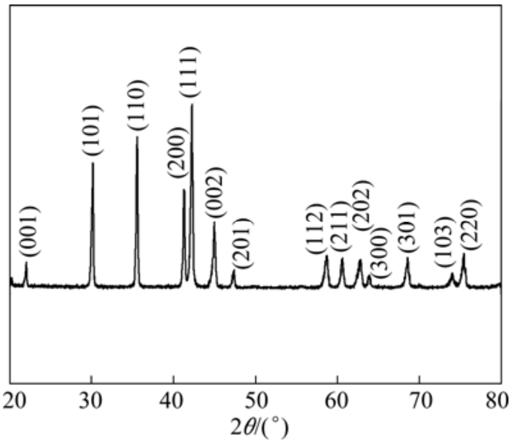

Fig.1 XRD pattern of $LaNi_{4.25}Al_{0.75}$ alloy

The lattice parameters and unit cell volumes of $LaNi_5$[5] together with calculated values for the $LaNi_{4.25}Al_{0.75}$ samples are presented in Table 1. It can be seen from Table 1 that unit cell dimension and lattice parameters of $LaNi_{4.25}Al_{0.75}$ increase slightly compared with $LaNi_5$.

Table 1 Unit cell volume and lattice constant of $LaNi_5$ and $LaNi_{425}Al_{0.75}$

Alloy	*a*/nm	*c*/nm	$V/(10^{-3}nm^3)$
$LaNi_5$	0.502	0.398	86.791
$LaNi_{4.25}Al_{0.75}$	0.504	0.405	89.260

$LaNi_{5-x}Al_x(x<1)$ alloy has $CaCu_5$-type hexagonal structure. La atoms occupy the La (0, 0, 0) Wyckoff site, two nonequivalent Ni atoms occupy the 2c (2/3, 1/3, 0) and the 3g (0, 0.5, 0.5) Wyckoff sites, Al atoms prefer to occupy the 3g sites in $LaNi_{5-x}Al_x$[8]. This was verified by total energy calculations[9]. CHEN et al[10−11] insisted that Al atom substituting for Ni atoms was in the 3g (0.5a, 0.5a, 0.75c) site in double unit cell of $LaNi_5Al_{0.5}$ and Al atoms were nonadjacent in $LaNi_{5-x}Al_x$ unit cell. So, Al atoms are not neighbor in $LaNi_{4.25}Al_{0.75}$ unit cell either, and maybe occupy in the 3g (0.5a, 0.5a, −0.5a, 0.5c), 3g (0.5a, 0.5a, −0.5a, 1.5c) and 3g (−0.5a, 0.5a, 0.5a, 1.5c) or 3g (−0.5a, 0.5a, 0.5a, 0.5c) sites in two neighbor HCP cells. As shown in Fig.2, the structure is composed of 4 La, 17 Ni and 3 Al atoms, i.e., 4La+17Ni+3Al= 4($LaNi_{4.25}Al_{0.75}$ unit cells)or 3$LaNi_4Al$ and 1 $LaNi_5$ unit cells.

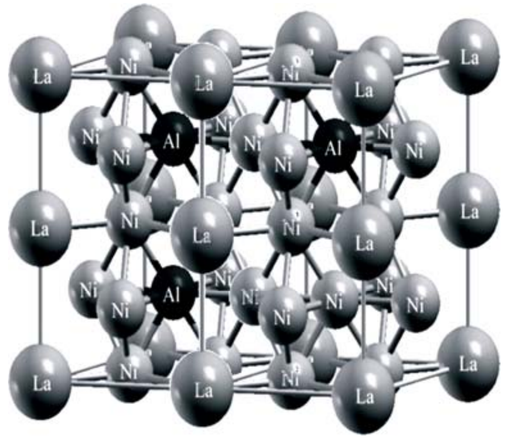

Fig.2 Structure of four-unit cell of $LaNi_{4.25}Al_{0.75}$

Table 2 lists atomic radii of La, Ni, Al and H[12], and interstice radii of polyhedron in $LaNi_5$ unit cell are presented in Table 3[13], those data indicate that all of interstice radii of polyhedron in $LaNi_5$ are clearly larger than the atomic radius difference of Ni and Al (0.018 nm), so 0.75 mol Al substituting Ni in $LaNi_5$ unit cell cannot change crystal structure, and unit cell dimension and lattice parameters of $LaNi_{4.25}Al_{0.75}$ increase slightly compared with $LaNi_5$, as seen in Table 1. The expansion is heterogeneous due to one without Al atom, the other three with Al atom in the four unit cells; meanwhile, the expansion in *c*-axis is larger than that in *a*-axis, indicating a lattice distortion in $LaNi_{4.25}Al_{0.75}$ crystal.

Table 2 Atomic radii of elements

Element	Atomic radius/nm
La	0.188
Ni	0.125
Al	0.143
H	0.046

Table 3 Interstice radii of polyhedron in $LaNi_5$ unit cell (nm)

Tetrahedron	Hexahedron	Octahedron	Twelve-face polyhedron
0.043	0.068	0.106	0.146

3.2 PCT curves

Fig.3 shows the hydrogen absorption PC isotherm(PCT) curves of $LaNi_{4.25}Al_{0.75}$ alloy after initial activation at 333, 353, 373 and 423 K. Hydrogen storage capacities of the alloy systematically decrease and absorption hydrogen plateau pressures significantly increase with increasing temperature. The function of plateau pressure (p_{eq}) and temperature (T) is $\ln p_{eq}=-4\,820/T+12.46$. The molecular formula of saturated hydride at 353 K is $LaNi_{4.25}Al_{0.75}H_{4.2}$. Compared with $LaNi_5H_6$[3], saturated hydrogen absorption capacity of $LaNi_{4.25}Al_{0.75}$ decreases by nearly 30% and plateau pressures is significantly lower.

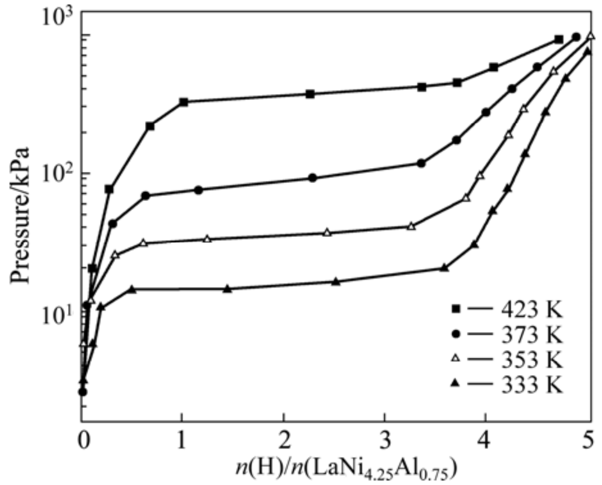

Fig. 3 Hydrogen absorption PC isotherms curves of $LaNi_{4.25}Al_{0.75}$ alloy after different initial activation temperatures

Lattice constants of $LaNi_{425}Al_{0.75}$ increase slightly compared with $LaNi_5$, the differences of a-axis and c-axis of the two alloys are 0.002 nm and 0.007 nm, respectively, and the increased amounts of a-axis and c-axis are less than the difference of atomic radii of Al and Ni (0.018 nm), as shown in Table 1 and Table 2. So, the substitution of 0.75 mol Al for Ni induces lattice distortion in $LaNi_{4.25}Al_{0.75}$ and causes interstice radii of polyhedron decrease. Some interstice radii of polyhedron in $LaNi_{4.25}Al_{0.75}$ alloy decrease so large that it is clearly shorter than hydrogen atomic radius. These interstitial sites (especially some tetrahedral and octahedral interstices) cannot accommodate hydrogen atoms, so hydrogen storage capacity of $LaNi_{4.25}Al_{0.75}$ alloy decreases compared with $LaNi_5$. GAO et al[8] found that the Fermi energies sharply increased in the order from $LaNi_5$ to $LaNi_{4.5}Al_{0.5}$ and $LaNi_4Al$ with the content of aluminum increasing. But electronegativities of these elements are H 2.1, Al 1.5, Ni 1.9 [11], the affinity of Al and H is stronger than that of Ni and H. So the hydrides of $LaNi_{4.25}Al_{0.75}$ is stable and its plateau pressures decrease compared with $LaNi_5$.

3.3 Hydrogen absorption kinetics curves

Hydrogen absorption kinetics curves of $LaNi_{4.25}Al_{0.75}$ alloy after 25 circles at 1 020 kPa (initial pressure of storage cell) are shown in Fig.4. 1 mol $LaNi_{4.25}Al_{0.75}$ can absorb over 4 mol H_2 in 60 s at 333 K and 373 K, but only absorb 3 mol H_2 in 100 s at 423 K, and hydrogen absorption rate decreases with increasing temperature.

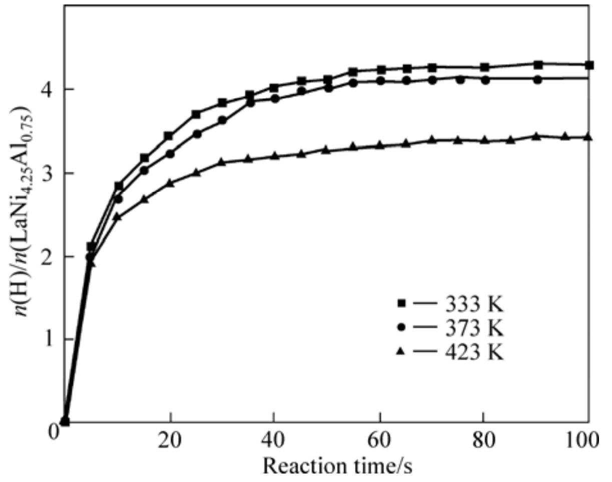

Fig.4 Hydrogen absorption kinetics curves of $LaNi_{4.25}Al_{0.75}$ alloy at different temperatures

Ni in $LaNi_{5-x}Al_x$ alloys can catalyze the reaction of alloy and H[4], so hydrogen absorption rates of these alloys are very rapid. More cracks and fissures are formed both on the surface and inside of the samples with the Al addition, which can shorten the hydrogen atom diffusion distance and provide more fresh surfaces for hydrogen atom association[13], so the alloy has rapid hydrogen absorption rate.

Fig.5 shows van't Hoff plot of $LaNi_{4.25}Al_{0.75}$ hydrogen absorption. The calculated enthalpy change and entropy change of $LaNi_{4.25}Al_{0.75}$ hydride formation are (−41.4±2.04) kJ/mol H_2 and (−106.0±2.57) J/(K·mol) H_2, and Gibbs free energy changes are all negative from 333 to 423 K. So, $LaNi_{4.25}Al_{0.75}$ alloy absorption hydrogen is exothermic reaction, hydrogen absorption rate decreases with increasing temperature.

3.4 Spontaneous combustion resistance performance

$LaNi_5$ hydride is easy to combust spontaneously in atmosphere gas in 10 circles, but $LaNi_{4.25}Al_{0.75}$ hydride cannot combust spontaneously in atmosphere gas after 25 circles.

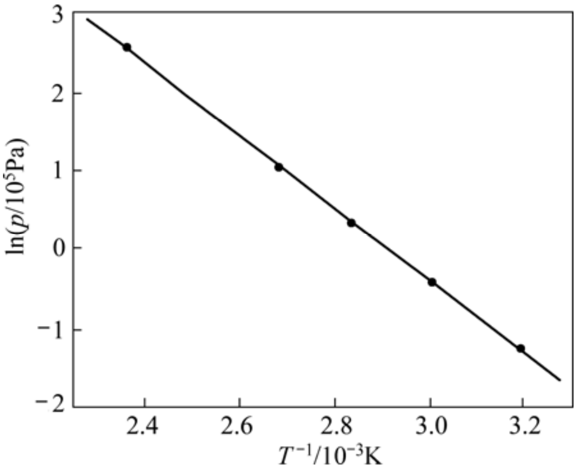

Fig.5 van't Hoff plots of $LaNi_{4.25}Al_{0.75}$ absorption hydrogen

FENG et al[6] investigated $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ during absorption/desorption cycling. They found that alloys with Al substituting exhibited excellent resistance to oxygen impurities due to the formation of Al_2O_3, which restricted the surface absorption of oxygen and prevented degradation; and Al element retarded the decomposition by restricting the exchange between La and Ni atoms in the neighboring sites. GIZA et al[13] insisted that Al accumulated on the grain boundaries and associated with segregated La to form porous oxide layer which protected the material from further corrosion and oxidation.

X-ray photoelectron spectroscopy(XPS) of $LaNi_{4.25}Al_{0.75}H_x$ hydride is shown in Fig.6. There are La_2O_3 and $La(OH)_3$, no Al_2O_3 on $LaNi_{4.25}Al_{0.75}H_x$ hydride surface.

Al atoms are surrounded by La and Ni atoms in $LaNi_{4.25}Al_{0.75}$ unit cell in Fig.2. Oxygen atom radius (0.73 nm) is significantly larger than interstice radius of tetrahedron or hexahedron in $LaNi_{4.25}Al_{0.75}$ unit cell, so Al atoms cannot be oxidized if $LaNi_{4.25}Al_{0.75}$ unit cell is not destroyed. In addition the electronegativities are La 1.0, Al 1.5, Ni 1.9 and H 2.1[12], respectively, so lanthanum atoms are firstly oxidized when $LaNi_{4.25}Al_{0.75}H_x$ connects with atmosphere gas. If Al_2O_3 is formed when $LaNi_{4.25}Al_{0.75}$ hydride connects with atmosphere gas, but it may be reduced by lanthanum atoms in neighbor sites, so Al_2O_3 is not found on the surface of $LaNi_{4.25}Al_{0.75}H_x$.

The particle diameter distribution plots of $LaNi_5$ and $LaNi_{4.25}Al_{0.75}$ alloys after 25 circles are shown in Fig.7. It can be seen that the particle diameters of $LaNi_5$ spread at a wider range of 5−60 μm and focus in 8−40 μm. Particle diameters of $LaNi_{4.25}Al_{0.75}$ spread 5−100 μm and focus in 20−70 μm. It is also found that $LaNi_5$ and $LaNi_{4.25}Al_{0.75}$ alloys easily pulverize after initial activation and hydrogen absorption, but $LaNi_{4.25}Al_{0.75}$

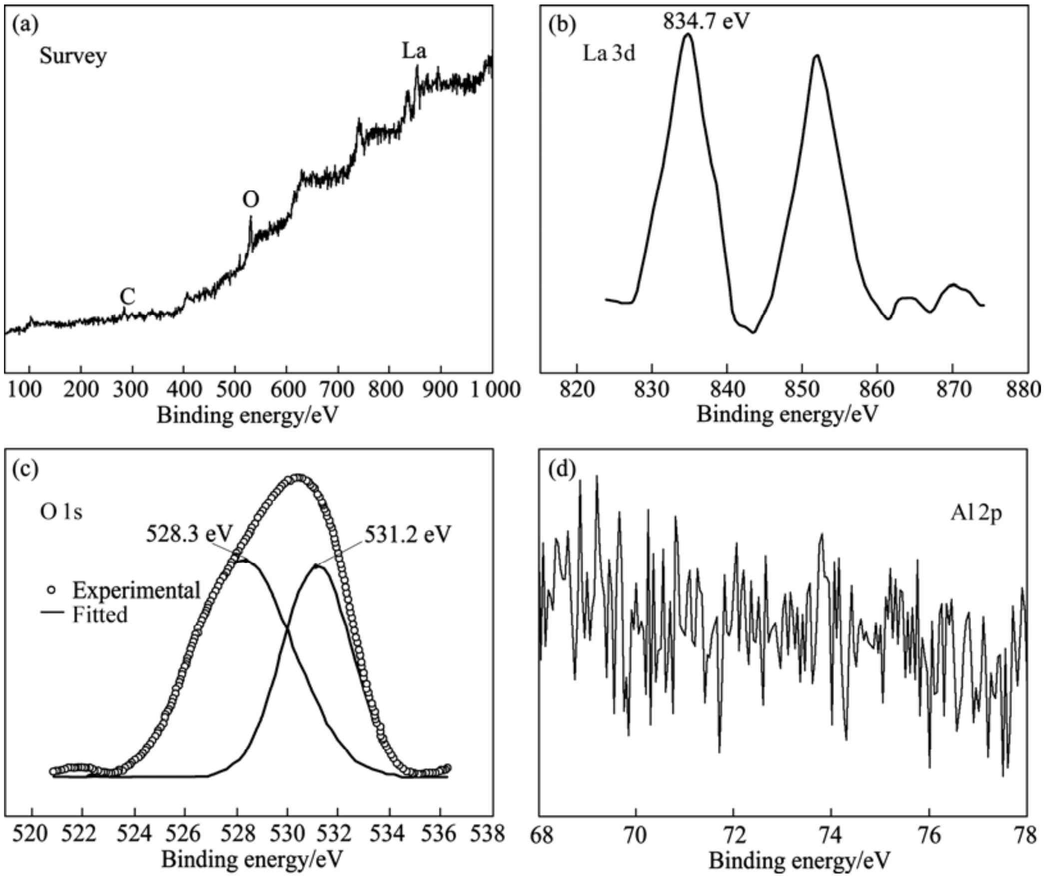

Fig.6 XPS of $LaNi_{4.25}Al_{0.75}H_x$

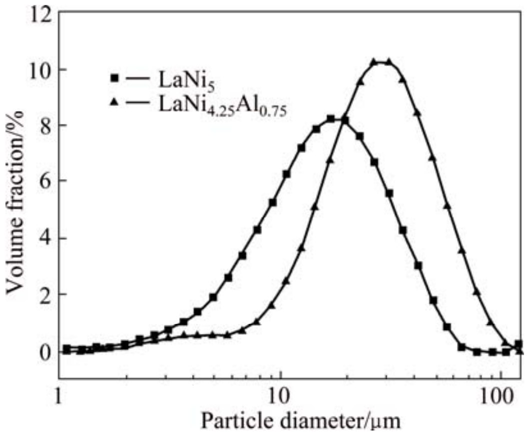

Fig.7 Plots of particle diameter vs volume fraction

alloy has better pulverization-resistant performance than $LaNi_5$ alloy.

CHENG et al[1] found that particle size of $LaNi_{4.25}Al_{0.75}$ alloy after 1 000 cycles was narrower (0.36−103 μm) compared with that after initial activation (0.78−301 μm). With the increase of volume fraction, mean diameter decreases from 34.81 to 11.34 μm, and the alloy was in homogeneous single phase with $CaCu_5$ structure and almost kept this structure even after 1 000 cycles.

Compared with $LaNi_5$, hydrogen storage capacity of $LaNi_{4.25}Al_{0.75}$ alloy decreases, so the lattice stress of $LaNi_{4.25}Al_{0.75}$ alloy decreases during the absorption/desorption hydrogen. On the other hand, the atomic radius difference between Ni and Al is 0.018 nm which is prominently larger than the expansion amount of *a*-axis (0.002 nm) and *c*-axis (0.007 nm), so there must exist compressive pre-stress in $LaNi_{4.25}Al_{0.75}$ alloy, which can counteract partial stress from absorption/desorption hydrogen. So, $LaNi_{4.25}Al_{0.75}$ alloy has an excellent pulverization-resistant property.

KIYONORI and KAZUHZRO[14] subjected $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ up to 2 000 absorption/desorption cycles at 293 K in super-high pure (99.99999%) hydrogen, and found that partial substitution of Ni by Al can reduce lattice stress which is caused during the cycle of absorption/desorption hydrogen. So Al substitution could improve the cycle stability.

4 Conclusions

1) The crystal structure of $LaNi_{4.25}Al_{0.75}$ alloy is $CaCu_5$ structure.

2) Hydrogen storage capacities of $LaNi_{4.25}Al_{0.75}$ systematically decrease and absorption hydrogen plateau pressures significantly increase with increasing temperatures.

3) The hydrogen absorption rate of the $LaNi_{4.25}Al_{0.75}$ alloy is very fast, and there is slight decrease with the increase of temperature.

4) $LaNi_{4.25}Al_{0.75}$ hydride cannot combust spontaneously in atmosphere gas after 25 cycles.

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$LaNi_{4.25}Al_{0.75}$ 合金的结构与储氢性能

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摘　要：采用 XRD、吸氢 PCT 曲线、吸氢动力学曲线、XPS 和粒径分析等测试方法，研究 $LaNi_{4.25}Al_{0.75}$ 合金的结构和储氢性能；推导 $LaNi_{4.25}Al_{0.75}$ 合金的四晶胞结构，分析 $LaNi_{4.25}Al_{0.75}$ 合金的结构与性能的内在联系。结果表明：$LaNi_{4.25}Al_{0.75}$ 合金具有快速吸氢性能和较好的抗燃烧能力，其吸氢平台压和温度之间的函数关系式为 $\ln p_{eq}=-4\,820/T+12.46$，合金的吸氢速率随着温度的升高而降低。

关键词：储氢合金；$LaNi_{4.25}Al_{0.75}$；微观结构；抗燃烧性

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