Properties of LaNi$_{4.3}$Al$_{0.7}$ applied in separating hydrogen from coke oven gas

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Abstract. Nowadays hydrogen as an important source of energy is still produced from fossil fuel processing largely, hence the separation of hydrogen from the gas mixture with high recovery ratio and purity arises as an important issue. In this paper we proposed a hydrogen recovery/production process from half-coke oven gas, and the material LaNi$_{4.3}$Al$_{0.7}$ was considered for use due to its low plateau pressure and good resistance to impurities. We use a Sieverts type volumetric apparatus to investigate the material properties,including P-C-T properties and hydriding/ dehydriding kinetics under different conditions. Based on the results obtained, the feasibility of using the material for gas separation purpose was discussed.

Introduction

China is the largest coke producer in the world, and the production of coke has been increasing. Making full use of coke has an important impact on resource. Coke oven gas is a byproduct of coal carbonization at low temperature ($<600\,℃$) which contains large amounts of N$_2$ (about 50%),H$_2$(about 20%)[1,2] . It is a research hotspot that how to separate and pure H$_2$ from the coke oven gas in recently years. Pressure swing adsorption(PSA),membranes, synthetic natural gas, methanol synthesis gas reformer preparation etc. have an widely used in high temperature coal carbonization, but none is feasible for H$_2$ coke oven gas[3].LaNi$_{4.3}$Al$_{0.7}$ which has a large hydrogen storage density, low equilibrium pressure and well anti-poisoning can absorb hydrogen at high pressure and release hydrogen when heating the alloy[4].Therefore, this paper discusses the feasibility of the LaNi$_{4.3}$Al$_{0.7}$ alloy separating hydrogen from coke oven gas.

Experimental details

The LaNi$_{4.3}$Al$_{0.7}$ in the present expermiment were prepared through melting method by the Beijing Genenal Research Institute for Nonferrous Metals (GRINM). A conventional Sieverts-type pressure-composition-temperature (P-C-T) apparatus developed by GRINM was used to measure the hydrogen absorption/desorption kinetic properties and the pressure-composition isotherm curves at different temperatures from 303 to 373K.
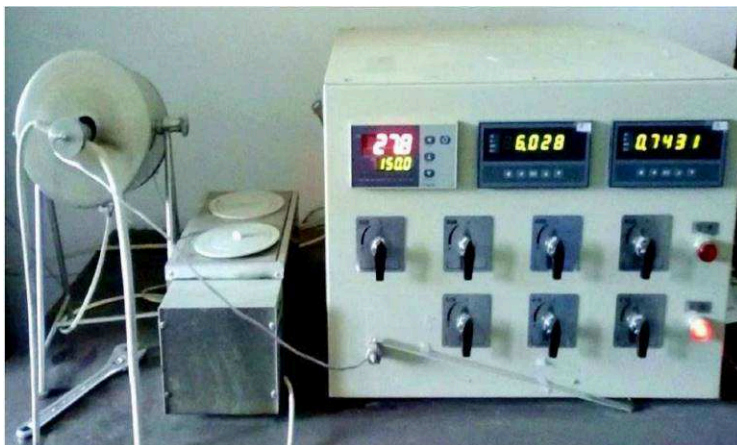

Fig. 1 P-C-T apparatus used in the work

In order to get large hydrogen content and fast kinetics,the LaNi$_{4.3}$Al$_{0.7}$ alloy had to be activated. The activation conditions are shown in Table 1.

Table 1 The activation conditions for hydriding and dehydriding

	Hydriding				Dehydriding
P[Mpa]	1	1	1	1	0
T[℃]	30	50	70	90	250
N[times]	8	7	6	5	

Results and discussion

After several cycles of hydrogen absorption and desorption, LaNi$_{4.3}$Al$_{0.7}$ alloy has received large hydrogen   content and fast kinetics.Curves of activation at different temperatures is shown in Fig.2.

(a) 30℃   (b)50℃

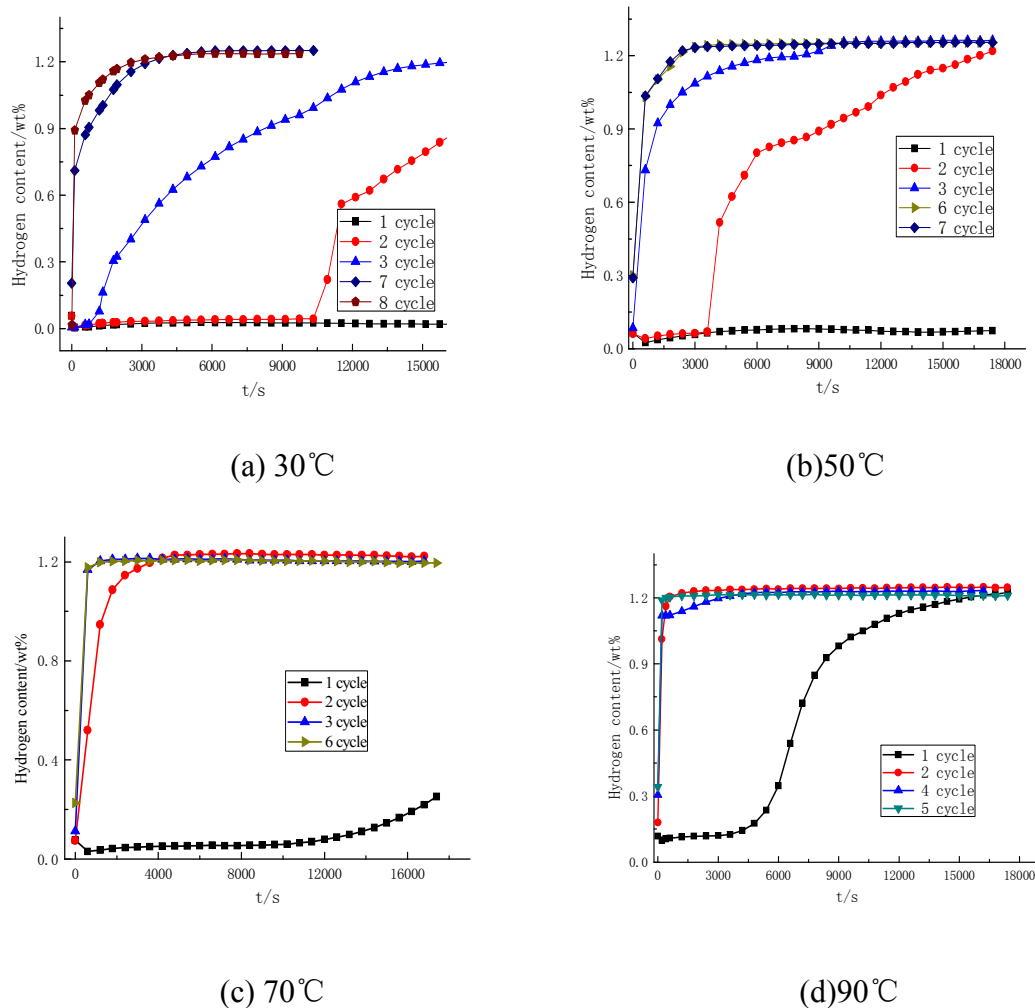(c) 70℃   (d)90℃

Fig.2 Activation curves at four different temperatures

It can be seen from Fig.2 and Table 1 that alloy needs 7,8,6and 5hydriding/dehydriding cycles to be completely activted at 30℃,50℃,70℃and 90℃,respectively.Therefore,we can conclude that the higher the temperature, the shorter time need to get fully activated.

After the alloy had been activated,it experienced 100 consecutive hydriding/dehydring cycles,during which we measured its kinetics and P-C-T properties.The experiment conditions are shown in Table 2.

Table 2 Experiment conditions for hydriding and dehydriding cycles

T[℃]	30		50		70		90	
Reaction process	Hydriding	Dehydriding	Hydriding	Dehydriding	Hydriding	Dehydriding	Hydri-ding	Dehy-driding
P[Mpa]	1	0	1	0	1	0	1	0
N[times]	100	100	100	100	100	100	100	100

The hydriding reaction rate curves is shown in Fig. 3.

(a) 30℃   (b)50℃

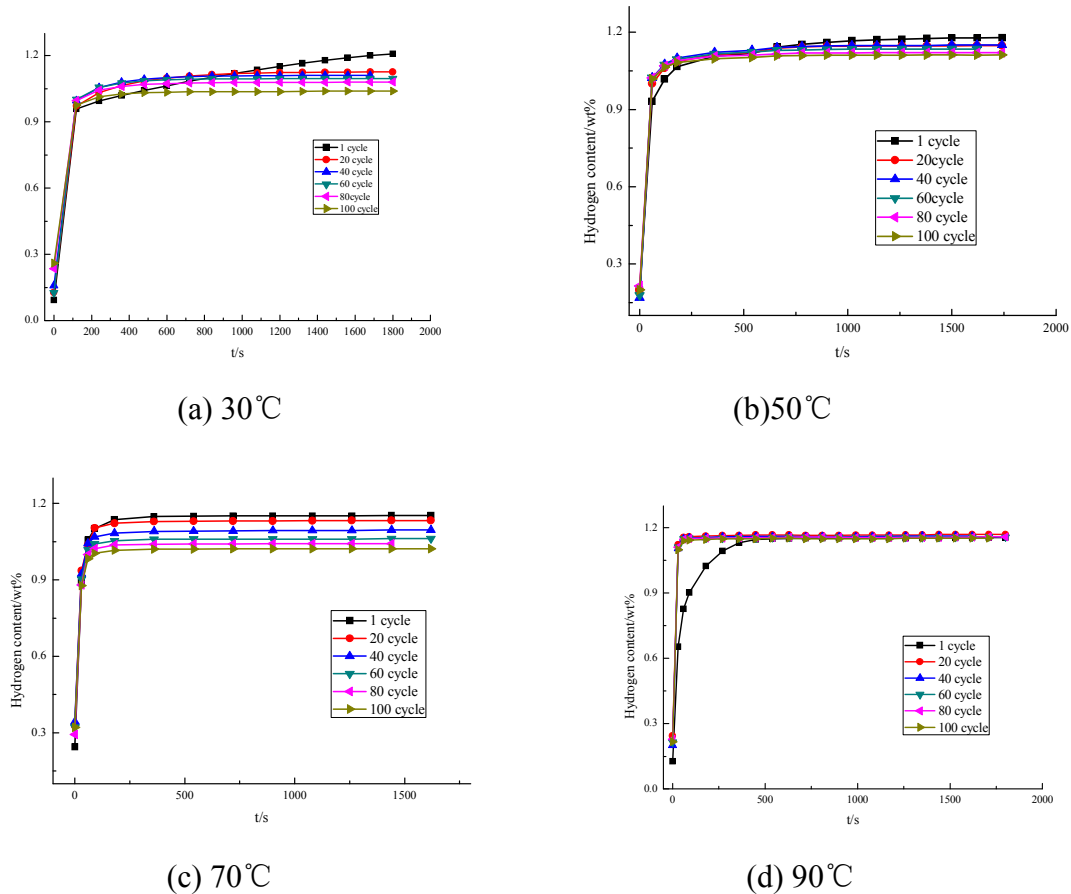(c) 70℃   (d) 90℃

Fig.3 The hydriding cycle kinetics curves at different temperature

From Fig.3, we can see that hydriding rate increases with the increase of cycle numbers at each temperature. The $LaNi_{4.3}Al_{0.7}$ alloy has fast hydriding kinetics and attains 90% maximum hydrogen content in 30s.However, the decrease of hydrogen content obviously after several cycles, which is no good for its practical application. P-C-T property is also one of the most important properties for hydrogen storage alloys. Therefore, the P-C-T curves in the initial cycle and after 100 cycles were also measured, and the results are presented in Fig. 4.

It can be seen from Fig.4 that the P-C-T properties are changed after 100 hydriding/dehydriding cycles at different temperatures. First, hydrogen content decreases after 100 hydriding/dehydriding cycles. Then, we can see from Table 3 that the dehydriding equilibrium is always lower that hydriding equilibrium, which is called hysteresis. Besides, both hydriding equilibrium and dehydriding equilibrium increase as temperature rises. These changes in P-C-T properties are not favorable for the hydrogen storage applications, as pointed out in a paper previously published by the authors [6].

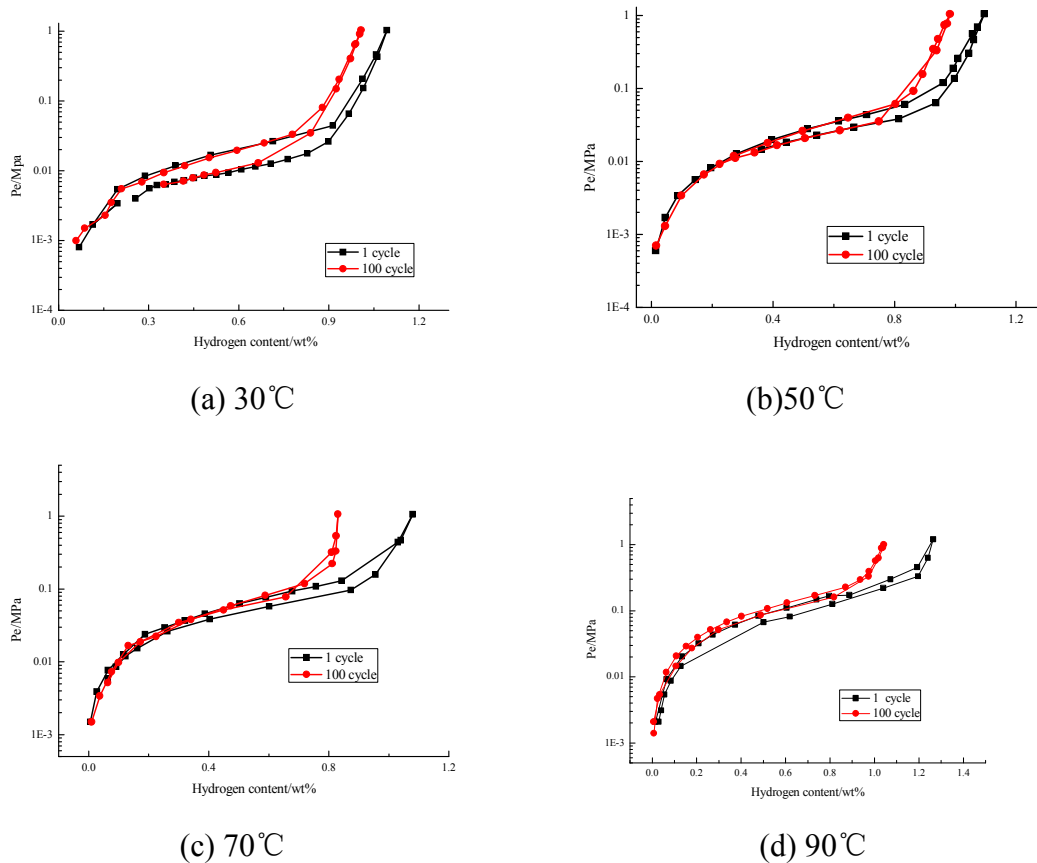(a) 30℃

(b)50℃

(c) 70℃

(d) 90℃

Fig.4 The P-C-T curves after 1 cycle and 100 cycles at different temperatures

Table 3 The change of hydriding/dehydriding equilibrium pressure after 100 cycles at different temperatures

T[℃]	30		50		70		90	
P_e[MPa]	P_{ea}	P_{ed}	P_{ea}	P_{ed}	P_{ea}	P_{ed}	P_{ea}	P_{ed}
1 cycle	0.0192	0.0110	0.0320	0.0228	0.0682	0.0523	0.1106	0.0815
100 cycle	0.0154	0.0089	0.0282	0.0208	0.0520	0.0515	0.1077	0.0912

Conclusions

The kinetics and P-C-T cycling properties of $LaNi_{4.3}Al_{0.7}$ alloy are measured at the temperature of 30℃, 50℃,70℃and 90℃, and the results can be summarized as follows:

1. The reaction rates of both hydriding processes increase with cycles, while the hydrogen content decreases with cycling.
2. The hydriding and dehydriding equilibrium pressure increases with temperature rises, while decreases for cycling.
3. $LaNi_{4.3}Al_{0.7}$ alloy has a large hydrogen content (about 1.2 wt. %) and fast reaction kinetics (about 30s) at 30℃, which can receive a good separation result for hydrogen separation from coke oven gas. Therefore, it is feasibility to use $LaNi_{4.3}Al_{0.7}$ alloy to separate hydrogen from coke oven gas.

Acknowledgements

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