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Pulverization, expansion of $La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ during hydrogen absorption–desorption cycles and their influences in thin-wall reactors

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ABSTRACT

The pulverization, expansion characteristics of $La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ and their influences in horizontal and vertical thin-wall reactors were investigated. Granulometric and SEM results revealed particle decay history and the transform from polydisperse to monodisperse state, then the reactor strain in both longitudinal and tangential directions was tested with packing fractions being 20–58.5 vol%. Results indicated that the longitudinal strain was less than the hoop strain; both increased with cycle numbers, initial packing fractions and hydrogen contents, while decreased from the lower to the upper positions. Horizontal reactors exhibited less strain than vertical ones; the former mainly bended and swelled while the latter bulged angularly. The strain increments were approximate linear along with cycles, while the absorption strain increments grew exponentially along with hydrogen contents. It is suggested that the optimal hydrogen contents for $La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ in the fully packed thin-wall reactors be less than 0.6 mol H/mol alloy whereas the packing fractions should not exceed 35 vol% for the case of hydrogen contents around 1.0 mol H/mol alloy.

1. Introduction

$La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ is one of the promising hydrogen storage alloys for applying in metal hydride heat pumps [1], and thin-wall reactors are preferred to reduce the system heat capacity and thermal resistance [2,3]. However, more than 45 MPa pressure would be exerted on vessel inner surfaces by alloy expansion of up to 27 vol% during absorbing hydrogen [4]; alloy pulverization and sedimentation with progressive cycles aggravate this disadvantage, and frequently lead to vessel fracture [5]. For the sake of solving this problem, it is essential to study the alloy pulverization and expansion characteristics, as well as their influences in thin-wall reactors.

However, available reports are quite scarce in this field. Nasako [4] found that the stress not only increased per cycle, but also continued to increase even after reactors' plastic deformation, while Saito [6] suggested that reactor deformation stopped growing once elastic deformation of the reactors occurred. Hydrogen contents vs. reactor surface strain was figured linear in Ao's [7] experiment on vertically placed $LaNi_5$ reactors; while McKillip [8] announced that strain remained low before 0.5 mol H/mol alloy and increased quickly until the maximum loading of 0.8 mol H/mol alloy. Aoki [9], Lynch [10] and Wang [11] also reported their work on hydride expansion and reactor deformation. Comparison of the above work shows that the strain on reactor surfaces is highly dependent on alloy types, reactor dimensions, placement, hydrogen

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Nomenclature

c	atom ratio, mol H/mol alloy
ΔH	reaction enthalpy, kJ/mol H_2
p	hydrogen pressure, Pa
t	reaction time, s
d_p	volume mean particle diameter, μm
n	cycle number
p_c	calibrating nitrogen pressure, Pa
ε	measured strain, με
ε_e	strain caused by alloy expansion, με
ε_p	strain caused by hydrogen pressure, με
ε_c	calibrating strain, με
$\Delta\varepsilon_e$	strain difference between complete hydrogen absorption and desorption, με
$\Delta\varepsilon'_e$	strain increment during absorption, με
ϕ	initial packing fraction, vol%

charges and alloy packing fractions; however, they have not been systematically discussed in these researches, which brought difficulties in evaluating and utilizing their conclusions. Consequently, more work should be done for supplement and improvement.

Aiming at characterizating $La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ pulverization and expansion properties during hydriding–dehydriding processes, as well as their influences, respectively, in horizontal and vertical thin-wall reactors, the decay of particle sizes was recorded and photographed in this paper; the surface strain in both longitudinal and tangential directions of the reactors designed for a prototype metal hydride heat pump [1] was measured at packing fractions of 20–58.5 vol%.

2. Alloy characterization

$La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ is a typical AB_5-type hydrogen storage alloy. It could absorb abundant hydrogen to form an interstitial or stoichiometric hydride. The reversible reaction is [12]

$$La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2} + \frac{c}{2}H_2 \leftrightarrow La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2} - H_c + \Delta H, \quad (1)$$

normally $c \leqslant 6.0$. In this paper, the alloy was prepared by high-frequency induction melting, then heat-treated under 1050 °C annealing for 6 h and quenched in ice water. The alloy density is 7.82 g/cm^3. Its P–C isotherms were measured as shown in Fig. 1.

Constant-volume method was adopted for measuring hydrogen absorption dynamics in Fig. 2. Results showed that the absorption process at 0 °C almost completed in 90 s with a final hydrogen content of 1.05 mol H/mol alloy, compared with that at 40 °C in 120 s with 0.98 mol H/mol alloy. Owing to the exothermic reaction, the reaction time was prolonged and the effective hydrogen contents were reduced with the increase in reaction temperatures. Considering that the designed work temperature for this alloy was within 20−50 °C [1], all the following tests were carried out at 40 °C with a charge pressure of 3.0–3.1 MPa to keep hydrogen contents around 1.0 mol H/mol alloy after hydriding processes.

3. Alloy pulverization

During hydriding processes, hydrogen atoms enter alloys' lattice and result in lattice expansion. This expansion brings large microstress and leads to alloy fragmentation [13], then induces macrostress to accumulate with progressive cycles owing to particle sedimentation and agglomeration [14]. Therefore, alloy pulverization is one of the most important factors to affect reactor reliability.

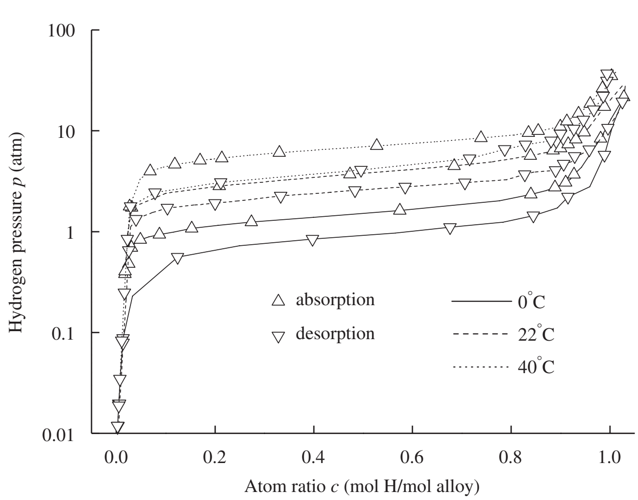

Fig. 1 – P–C isotherms.

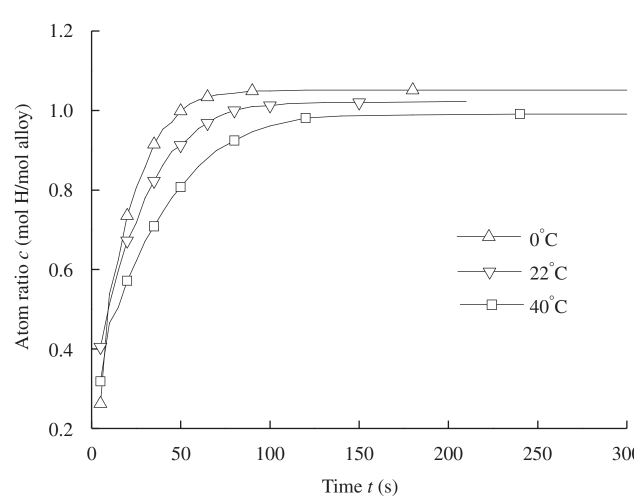

Fig. 2 – Hydrogen absorption dynamics.