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Study of a hydride forming system by thermogravimetry. Hydriding characteristics of $LaNi_5$ mixed with nickel powders

M. El Hammioui *[,a,1] L. Belkbir[a] and N. Gerard[b]

[a] *Laboratoire de la Réactivité des Systèmes Solides–Gax, Faculté des Sciences, Université Mohammed V, B.P. 1014 Rabat (Morocco)*

[b] *Laboratorie de Recherche sur la Réactivité des Solides, Faculté des Sciences Mirande, B.P. 138, 21004 Dijon-Cedex (France)*

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Abstract

$LaNi_5$ powder was mixed with metallic nickel powders. The powdered and compacted mixtures were subjected to hydriding–dehydriding cycles. Hydrogen absorption occurs by a nucleation and growth process and can be strongly changed by altering the particle size of the nickel powder. When this is very small, hydridation is complicated by bad hydrogen flow.

INTRODUCTION

The metallic compound $LaNi_5$ is of considerable interest because of its ability to react rapidly and reversibly with large quantities of hydrogen (six hydrogen atoms per formula $LaNi_5$) at ambiant temperature and moderate pressures. In addition to its desirable properties for practical applications, the $LaNi_5$ system is considered to be a prototype material for hydrogen storage.

During the hydriding–dehydriding cycles, a grain fragmentation of the sample occurs until the grain size is about 10 μm [1, 2]. Owing to the heat (-32 kJ bar mol H_2) which accompanies the hydriding reaction, the fine particle bed involves a higher temperature gradient. If this gradient is large enough, it is conceivable that heat transfer could be the limiting process. The temperature level reached can decrease the global hydriding rate by its

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* Corresponding author.

[1] Permanent address: Laboratorie de Chimie Physique, Faculté des Sciences Semlalia, Université Cadi Ayyad, B.P. S 15, Marrakech, Morocco.

action on thermodynamics terms. This explains why proposed models describing the hydrogen absorption mechanism are wildly divergent. Moreover, from an engineering viewpoint, the fine powder of the alloy can be scattered and may cause great damage to the system where hydrogen is used by repeated hydriding–dehydriding cycles.

Several approaches have been made to minimise the temperature gradient in the hydride bed. The thermal ballasting technique was used by several investigators [3–6] and consists of increasing the heat capacity of the sample by mixing $LaNi_5$ with an inert metallic ballast. When the mixture is compacted, the scattering of the fine powder produced can be prevented. By increasing the ballast fraction, isothermal conditions could be approached without having to conduct heat out of or into the reactor. Rudman [7] has reported that an adequate isothermal approximation requires a ballast fraction of 97.5 wt%.

In spite of that, a scatter in the hydriding rates still exists. For example, Goodell and Rudman [5] found very rapid hydrogen absorption, while in an earlier work carried out by us, no significant difference was observed between pure $LaNi_5$ and $LaNi_5$–Ni mixture [6].

In order to elucidate the reason for this disagreement, the present work reports the role played by the metallic ballast, which is still poorly understood, in the case of the hydriding of the powdered and compacted mixtures.

APPARATUS AND SAMPLES

The hydrogen uptake was carried out in a high pressure microbalance, which has been described before [8], using powder or block mixtures of 30 mg of pure $LaNi_5$ with nickel powders. According to Rudman [7], the mixtures contain 2.5 wt.% of $LaNi_5$. Three different powders were used (see Table 1). The samples (powdered mixtures and pellets) were outgassed three times at 150°C under 0.1 MPa hydrogen pressure. The hydrogen used is "U" quality supplied by l'Air Liquide.

TABLE 1

Nickel powder characteristics [a]

Ni powder	Granulometry/μm	Shape of particles
Ni(I)	5–15	Spherical
Ni(II)	150–200	Irregular
Ni(III) [a]		Dentritical

[a] Ni(III) is the same powder used in ref. 5.

EXPERIMENTAL RESULTS AND DISCUSSION

The hydrogen uptake of the powdered samples under 0.3 MPa hydrogen pressure at 25°C is reported in Fig. 1. A curve of pure $LaNi_5$ is also reported for comparison. All the curves are sigmoidal. The inflection point changes from $n_H = 3$ for $LaNi_5$ and $LaNi_5$–Ni(I) to $n_H = 1$ for $LaNi_5$–Ni(II). In the same way, the hydrogen uptake of compacted samples is reported in Fig. 2 in the same conditions. This figure shows a sigmoidal curve for $LaNi_5$–Ni(I) but continuously speed-decreasing curves for $LaNi_5$–Ni(II) and $LaNi_5$–Ni(III).

The change in the shape of the curves have been interpreted by a nucleation and growth process [9, 10]. The nucleation mechanism can proceed differently on the surface of the $LaNi_5$ particles. A direct observation of nucleation and growth is impossible since the hydride phase cannot be maintained as a metastable phase in the $LaNi_5$–H_2 system. As a consequence, nucleation and growth can only be deduced from kinetic curves. According to Delmon [10], the transformation ratio α is expressed

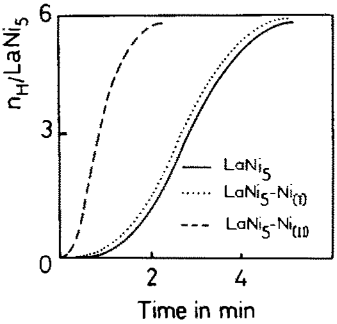

Fig. 1. Hydride formation curves at 25°C under 0.3 MPa hydrogen pressure for the $LaNi_5$–Ni mixtures (powders).

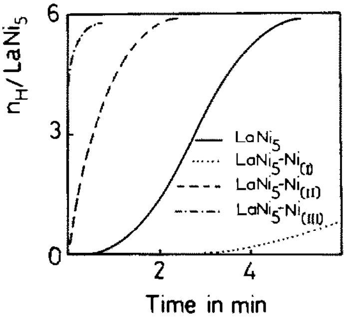

Fig. 2. Hydride formation curves at 25°C under 0.3 MPa hydrogen pressure for the $LaNi_5$–Ni mixtures (pellets).

by

$$\alpha = 1 - (1-\tau)^3 - 3\,\xi_0^\tau\,(1-\xi^2)\exp\left[-B_{s(i)}\frac{\tau^2-\xi^2}{1-\xi}\right]\mathrm{d}\xi \tag{1}$$

$$\tau = (k_i/a_0)t \tag{2}$$

$$B_{s(i)} = \pi a_0^2 \nu_0 \tag{3}$$

α is defined as the number of hydrogen fixed at time t compared with the number fixed when the reaction is complete ($\alpha = n_H/6$). k_i represents the interfacial rate in the $LaNi_5$ particles having a_0 as mean radius and $B_{s(i)}$ is the quarter of the mean number of nuclei. ν_0 is the mean density of the nuclei on the surface of $LaNi_5$ particles.

When $B_{s(i)}$ is high ($B_{s(i)} \to \infty$), the term under integration in eqn. (1) tends to zero and this equation is reduced to

$$1 - (1-\alpha)^{1/3} = (k_i/a_0)t \tag{4}$$

The reaction in this case occurs by the formation, from many nuclei, of a continuous layer in which the regulating step is the interface progress in spherical symmetry.

When $B_{s(i)}$ is less important, the reaction occurs by nucleation and growth of many dispersed nuclei which coalesce subsequently. This let us envisage the existence of an incubation period t_1, after which the nuclei join each other and form a continuous layer. Then, the hydride formation curves could be expressed by eqn. (4). Figures 3 and 4 report the evolution of $1-(1-\alpha)^{1/3}$ versus time for powders and pellets respectively. A good linearity is obtained after the incubation period.

The main result shown in Fig. 1 is that there is a slight difference between $LaNi_5$–Ni(I) and pure $LaNi_5$. This does not mean that heat transfer no longer controls the hydriding process. On the contrary, the increase in the formation rate, by heat capacity, is counterbalanced by the fact that the

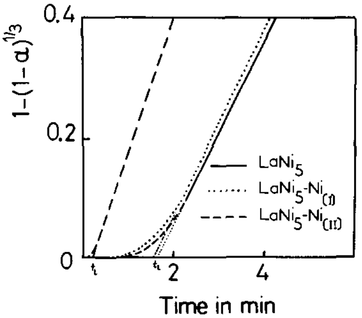

Fig. 3. Transformation of the hydride formation curves according to eqn. (4) ($1-(1-\alpha)^{1/3} = (k_i/a_0)t$) at 25°C under 0.3 MPa hydrogen pressure for the $LaNi_5$–Ni mixtures (powders).

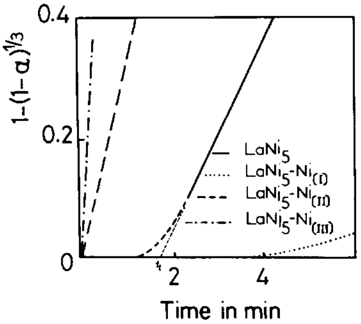

Fig. 4. Transformation of the hydride formation curves according to eqn. (4) $(1-(1-\alpha)^{1/3} = (k_i/a_0)t)$ at 25°C under 0.3 MPa hydrogen pressure for the $LaNi_5$–Ni mixtures (pellets).

hydrogen flow is hindered in the fine particle bed of the $LaNi_5$–Ni(I) sample. Hydrogen flow is seriously complicated when this sample is compacted into pellets (Fig. 2). Pellets absorb hydrogen faster than powders when the particle size of the ballast is high. Goody et al. [4] have reported that powders react faster than pellets, but without giving any information about the ballast used.

A surface segregation model [11] explained very successfully the great reactivity of $LaNi_5$. The surface segregation occurs by the presence of oxygen. A top layer rich in La-oxide is formed. The Ni atoms are kept metallic and cluster together to form microcrystals in a subsurface layer. The segregation provides catalytically active sites for the H_2 dissociation on the microcrystals (Ni). According to Gerard [12], the number of active dissociation sites determines the number of active nucleation sites.

Taking into these interpretations, the change in the reactivity of $LaNi_5$ in the series of samples can be explained by the fact that the hydriding rate, which is improved by increasing heat capacity, is enhanced in the case of compacted samples by the presence of more dissociation sites. Thus, by compacting $LaNi_5$ with Ni metallic powder, the metal becomes encrusted on the very hard $LaNi_5$ surface, for example by mechanical abrasion. The encrusted nickel could play the role of new active dissociation sites which generate new active nucleation sites. When the particle size of the ballast is very small, these advantages are counterbalanced by bad hydrogen flow.

CONCLUSIONS

Hydridation of dispersed $LaNi_5$ into a large quantity of metallic ballast was carried out under isothermal conditions. Hydride formation occurs by a nucleation and growth process. The number of nuclei appearing depends on the morphology of the ballast used. Choice of ballast must be taken into account for potential applications.

REFERENCES

1 L. Belkbir, E. Joly and N. Gerard, Int. J. Hydrogen Energy, 6(3) (1981) 285–294.
2 H. Uchida, H. Uchida and Y.C. Huang, J. Less-Common Met., 101 (1984) 459–468.
3 M. Ron, D. Gruen, M. Mendelsohn and T. Sheft, J. Less-Common Met., 74 (1980) 445–448.
4 A.J. Goody, D.G. Stokes and J.A. Gazzillo, J. Less-Common Met., 91 (1983) 149–158.
5 P.D. Goodell and P.S. Rudman, J. Less-Common Met., 89 (1983) 117–125.
6 C. Bayane, M. El Hammioui, E. Sciora and N. Gerard, J. Less-Common Met., 107 (1985) 213–219.
7 P.S. Rudman, J. Less-Common Met., 89 (1983) 93–110.
8 N. Gerard, C. Bayane and M. El Hammioui, Thermochim. Acta, 82 (1984) 171–177.
9 V.V. Boldyrev, M. Bulens and B. Delmon, The Control of the Reactivity of Solids, Elsevier, Amsterdam, 1979.
10 B. Delmon, Introduction to Heterogeneous Kinetics, Technip, Paris, 1969.
11 L. Schlapbach, A. Seiler, H.C. Seigmann, T.V. Waldkirch, and P. Zürcher, Int. J. Hydrogen Energy, 4 (1979) 21–28.
12 N. Gerard, J. Less-Common Met., 131 (1987) 13–23.