Journal of Alloys and Compounds 293–295 (1999) 374–378

Improvement of the activation stage of $MmNi_{4.7}Al_{0.3}$ hydride-forming alloys by surface fluorination

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Abstract

The formation of a thin Ni-rich film on the surface of $LaNi_5$-type alloys by surface fluorination facilitates hydrogen molecule dissociation and protects the material surface from oxidation. In this work we present the improvement obtained in the first hydrogen absorption reaction of massive and powdered $MmNi_{4.7}Al_{0.3}$ samples treated with HF after melting. In the case of massive samples the duration of the activation stage of untreated specimens is about eight times longer than with HF-treated specimens. Fluorinated powdered samples also show a reduction of one order of magnitude in the activation time when they are compared with as-melted and crushed samples. Using a step model to analyze the hydrogen absorption kinetics of untreated and HF-treated powdered samples, it was possible to identify the limiting processes in each case. Untreated samples show hydrogen absorption kinetics limited by surface-related processes: chemisorption and/or surface diffusion. In the case of HF-treated specimens the analysis of the absorption kinetics shows that diffusion in the bulk is the slower process. So, a higher hydrogen pickup rate in samples treated with the proposed HF treatment is possible only by improvement of the bulk properties. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Fluorination; Kinetics; $LaNi_5$

1. Introduction

$LaNi_5$-type alloys are being studied extensively because of their adequate properties for potential use in hydrogen-related technology, in particular due to their high hydrogen storage capacity and the possibility of tailoring to select the hydride-forming pressure at room temperature. While the use of Mm (Mm: mishmetal) instead of La significantly lowers the cost without substantial change in the hydrogen storage properties, the replacement of Ni by Al reduces the plateau pressure [1,2]. Therefore, several applications for hydrogen storage, compression or purification are possible with a convenient selection of the Al concentration in the $MmNi_{5-x}Al_x$ alloy.

Despite the positive characteristics mentioned above, there is a problem to overcome before these alloys can be employed in the hydrogen industry: when the as-melted alloy is exposed to air a thin surface oxide film is generated, making hydrogen uptake during the activation process difficult. Conventional methods to avoid or minimize this problem are manipulation of the material after alloying under a protective atmosphere, or performing the activation stage at a pressure and temperature higher than the equilibrium values. Complicated procedures in the first case and over-dimensioned vessels where the material will be used in the second increase the final cost.

There are several reports of experimental techniques related to the chemical etching of the surface of $LaNi_5$ samples using fluoride-based solutions [3–5]. As a result of the chemical reaction, a brittle and easily removable LaF_3 layer is formed on the surface while an underlying Ni-rich film is obtained by segregation. This thin Ni-rich film is responsible for the observed improvement of the activation process, even if the treated sample is exposed to air. Recently, the use of three fluoride-based solutions (HF, KHKF, NH_4F) was evaluated on $LaNi_5$ samples and HF treatment was selected due to a higher La/Ni ratio in the surface, higher repeatability and lower surface contamination [5].

In this work we present the results of applying chemical etching to $MmNi_{4.7}Al_{0.3}$, in particular the study of the hydrogen absorption kinetics during the activation process. Powdered and bulk samples were studied.

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PII: S0925-8388(99)00405-3

2. Experimental details

$MmNi_{4.7}Al_{0.3}$ samples were obtained by melting the components in stoichiometric proportions under ultra-pure argon atmosphere in an arc furnace with a copper crucible. The main composition of Mm (Alfa Inc.) is (wt.%): 56 Ce, 18 La, 13 Nd, 5 Pr, 2 Fe, 2 Y. After melting, annealing treatment in Ar atmosphere at 900°C for 12 h provides a uniform Al concentration throughout the whole sample. Fig. 1 shows the X-ray powder diffraction pattern of as-melted and annealed samples obtained with Cu Kα radiation. Fig. 2a,b show Al concentration patterns obtained with the energy dispersive spectroscopy (EDS) facility of the scanning electron microscope (SEM) before and after thermal treatment, respectively. Fig. 3 shows hydrogen absorption/desorption pressure–composition isotherms of as-melted and annealed samples at 30°C measured with an experimental setup developed in our laboratory [6].

Sharper peaks in the X-ray diagram (Fig. 1), the absence of Al segregation in the EDS analysis (Fig. 2b) and strong reduction in the plateau slope (Fig. 3) are related to the compositional homogenization of Al after annealing [7,8].

Some samples were chemically etched for 5 h with 4 M hydrofluoric acid (HF) with 2:1 gravimetric proportion of the solution/alloy ratio. Fig. 4 shows SEM photographs of (a) as-melted and non-activated, (b) as-melted and activated and (c) HF-treated and non-activated powdered $MmNi_{4.7}Al_{0.3}$ specimens. The main differences observed are related to the size and surface of grains. While the surface of the grains of untreated and non-activated samples shows few macroscopic defects, many cracks appear after the first hydrogen absorption/desorption cycle due to sample crushing induced by hydrogenation. Fig. 4c shows that the grains of non-activated HF-treated specimens present hard surface roughness, as reported previously for similar chemical etching [4,9].

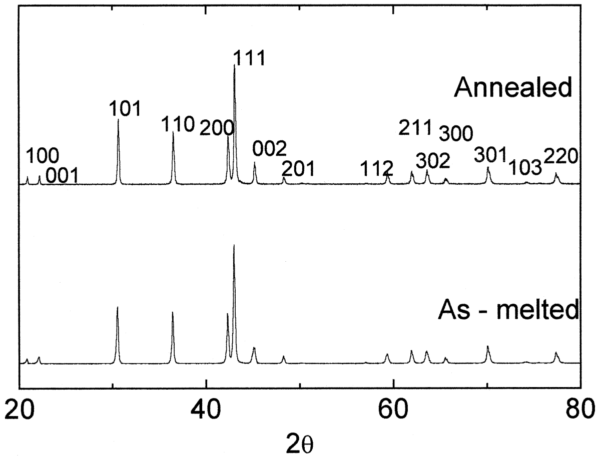

Fig. 1. X-ray diffraction pattern of as-melted and annealed $MmNi_{4.7}Al_{0.3}$ powdered samples.

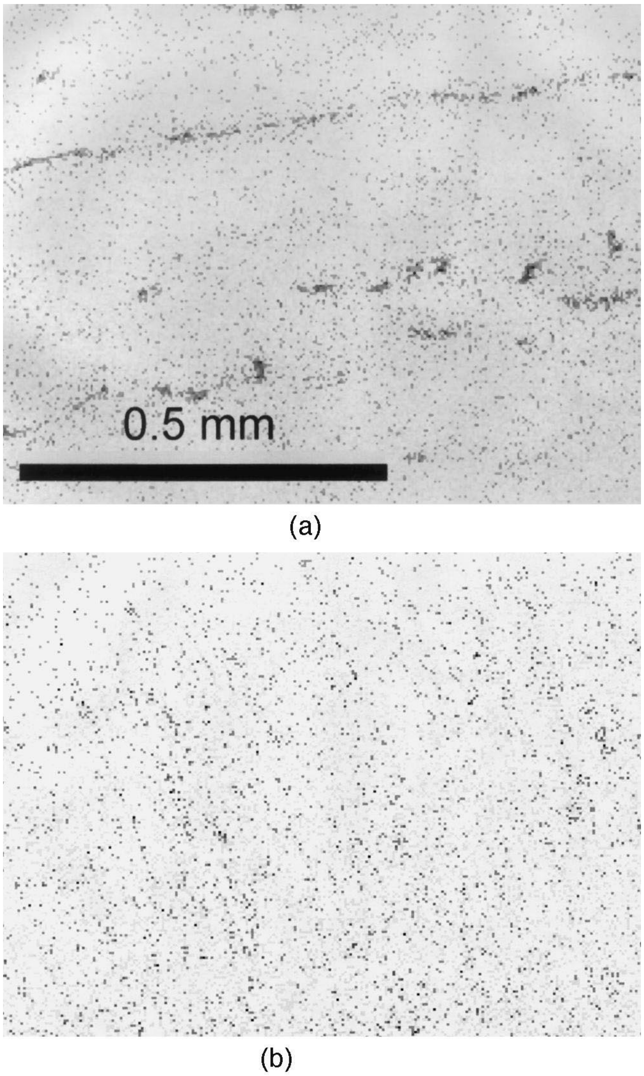

Fig. 2. Aluminum EDS pattern of (a) as-melted and (b) annealed $MmNi_{4.7}Al_{0.3}$ samples. Darker regions correspond to higher Al concentration.

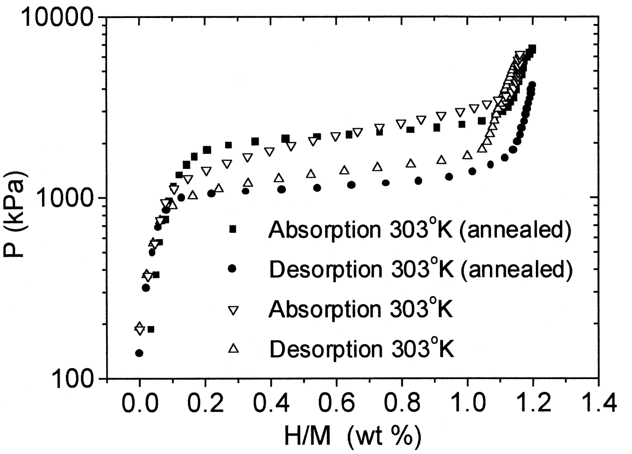

Fig. 3. As-melted and annealed $MmNi_{4.7}Al_{0.3}$ absorption/desorption pressure–composition isotherms at 303 K.

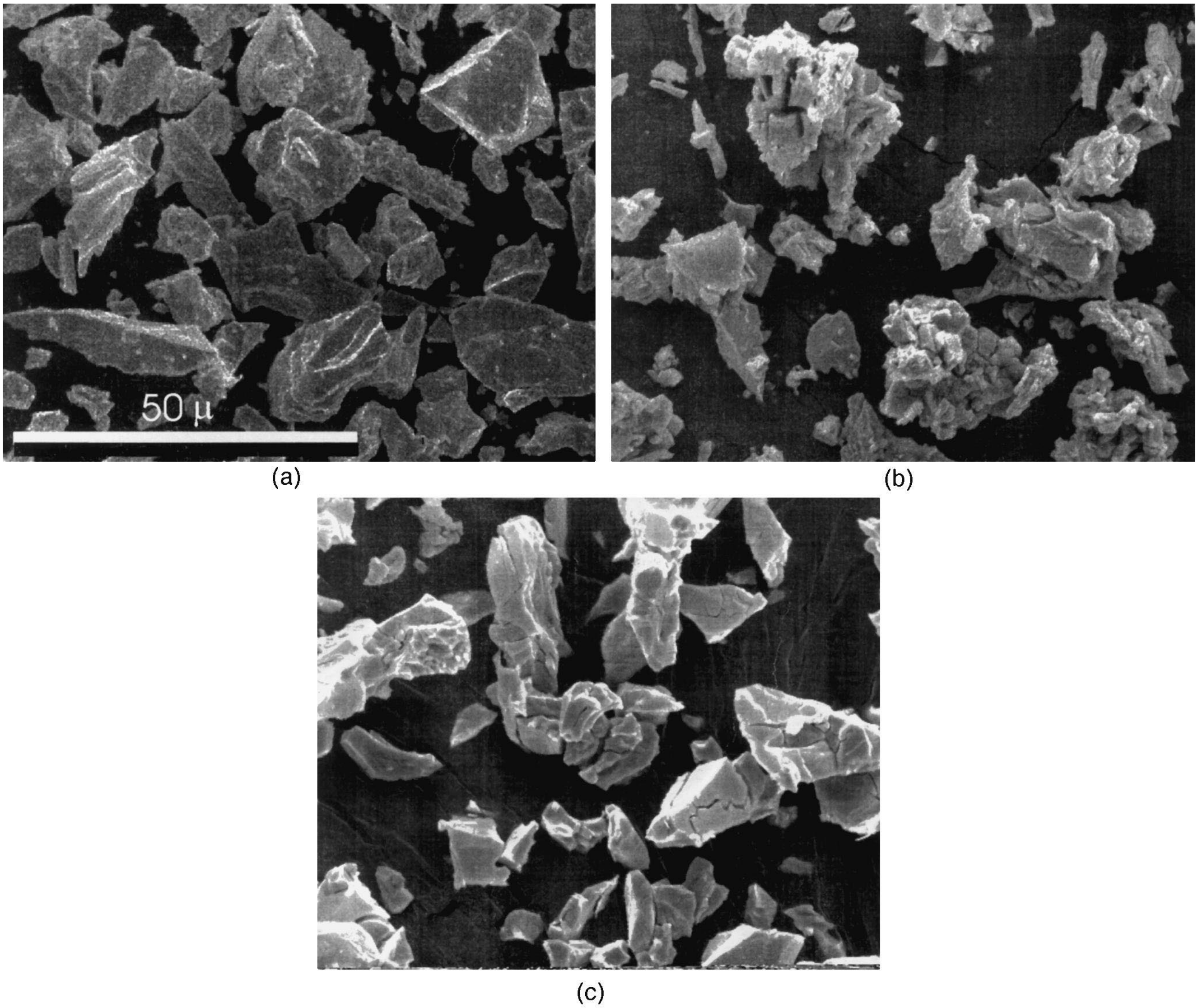

Fig. 4. SEM photographs of $MmNi_{4.7}Al_{0.3}$: (a) untreated powdered sample; (b) sample (a) after activation; (c) HF-treated specimen before activation.

Activation kinetics and the first hydrogen absorption/desorption cycles were measured using Sievert-type equipment. Each sample was placed in the reactor at constant temperature and at a selected initial pressure. A PC-based data acquisition system monitors and controls the experimental parameters. A detailed description of the experimental setup can be found elsewhere [7]. All the hydrogen absorption kinetics presented in this work were measured at 30°C, starting with an initial pressure of 2000 kPa.

3. Results

To analyze the potential applications of the chemical treatment on the material of interest we performed hydrogen absorption kinetics measurements of untreated and HF-treated $MmNi_{4.7}Al_{0.3}$ samples, both in massive and powdered form.

Fig. 5 shows the hydrogen absorption kinetics during the activation process of untreated and HF-treated massive samples. It can clearly be observed that the incubation time of this stage in the untreated specimen is about eight times greater than that in the HF-treated sample. While HF treatment generates a Ni-passivated surface that results in a convenient entrance for hydrogen, exposure to air of untreated surfaces results in the development of oxide phases in the surface that restrict dissociation of the hydrogen molecule and diffusion through the film [10].

To study the influence of the surface/bulk ratio in the activation stage for treated and untreated samples we started with two untreated massive samples powdered at room temperature under a protective Ar atmosphere: one was exposed to air and activated and the other was HF-treated, exposed to air and activated. Fig. 6 shows the

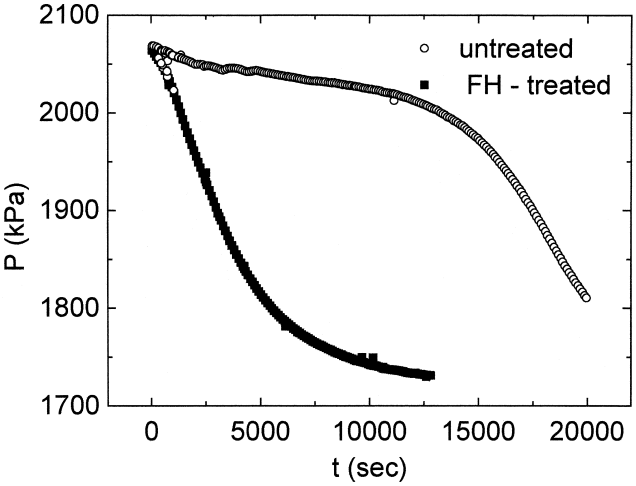

Fig. 5. Hydrogen absorption kinetics of massive untreated and HF-treated $MmNi_{4.7}Al_{0.3}$ samples.

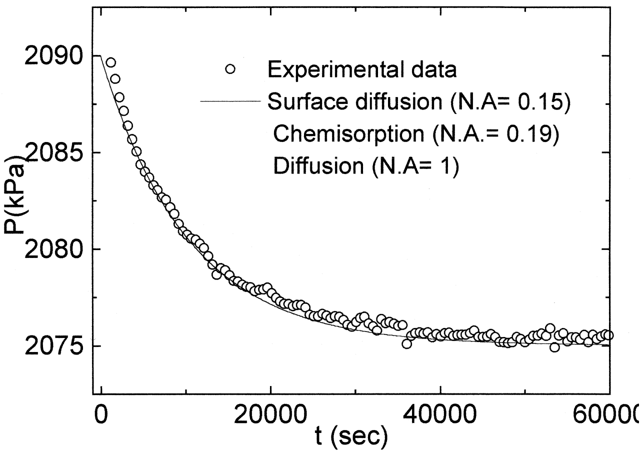

Fig. 7. Hydrogen absorption kinetics of powdered untreated $MmNi_{4.7}Al_{0.3}$. Curve fitting corresponds to the assumption of chemisorption as the limiting stage. The normalized area (N.A.) for the other possible assumptions is also included.

hydrogen absorption kinetics of these samples. While the HF-treated specimen activates in a few minutes, the untreated sample needs about 14 h to reach the same final hydrogen concentration, one order of magnitude greater. The crushing process significantly increases the surface/bulk ratio, adding more possibilities for hydrogen uptake. This is observed in the case of the untreated sample where hydrogen uptake began before the massive sample. Although massive samples initially offer few paths for hydrogen pick up, the absorption process accelerates when new oxide-free surfaces are generated in the cracks that appear when the hydride phase develops due to the different molar volume of the coexisting phases. In the case of powdered untreated samples, cracks do not appear due to the small grain size and the oxidized surfaces dominate the whole activation process, resulting in a longer activation time for completion of the process.

To analyze the absorption kinetics we will consider the model proposed by Martin [11] which takes into account hydrogen chemisorption, its surface diffusion, bulk diffusion and hydride formation stages using an experimental setup like ours. Because each process is related to a different functional law, the limiting stage in the hydrogen absorption process can be identified from the best fitting curve obtained. To determine the best fit we defined a parameter, called the normalized area (N.A. in the figure captions), obtained as the integration of the differences between experimental data and each fitting function in the period of measurement and normalized with respect to the worst fit. Fig. 7 shows that the best fit is obtained when surface-related processes (chemisorption and surface diffusion) are assumed to govern the absorption kinetics in a powdered untreated specimen.

Fig. 8 shows that bulk diffusion is the limiting stage during hydrogen absorption of a powdered HF-treated

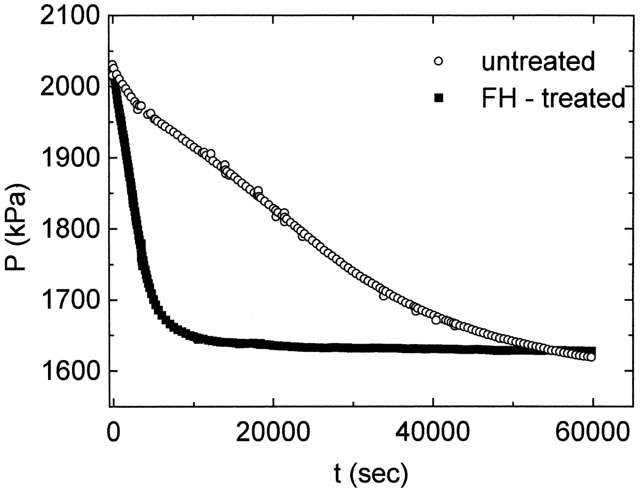

Fig. 6. Hydrogen absorption kinetics of powdered untreated and HF-treated $MmNi_{4.7}Al_{0.3}$ samples.

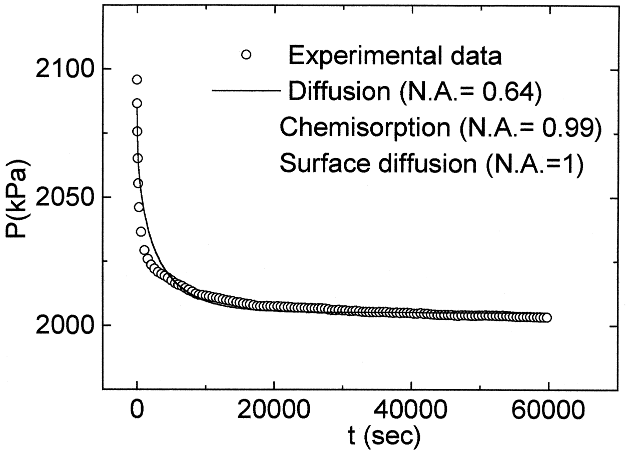

Fig. 8. Hydrogen absorption kinetics of powdered HF-treated $MmNi_{4.7}Al_{0.3}$. Curve fitting corresponds to the assumption of bulk diffusion as the limiting stage. The integral parameters for the other possible assumptions are also included.

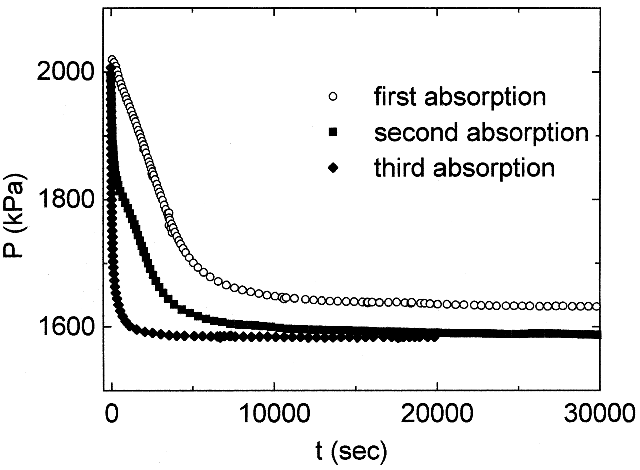

Fig. 9. First hydrogen absorption/desorption cycles.

sample. This result agrees well with a previous report that studied the hydrogen pick-up of surface-improved $MmNi_{4.7}Al_{0.3}$ [10].

Several hydrogen absorption–desorption cycles were performed on HF-treated samples to test the efficiency of the activation process. Fig. 9 shows that, after the first three cycles, the hydrogen uptake strongly improves and near-maximum hydrogen storage capacity is reached.

4. Conclusions

The oxide film formed on the surface of as-melted (annealed or not) $MmNi_{4.7}Al_{0.3}$samples when exposed to air hinders hydrogen absorption during the activation process. We have shown that improvement in the absorption kinetics can be obtained with a surface fluorination technique using HF as chemical agent. The most important improvements observed are the reduction of the incubation time and the possibility of sample exposure to air without losing the fast absorption kinetics.

Measurements of the activation process in massive samples show that the important reduction in incubation time can avoid the crushing stage performed before the use of the alloys in any device. This means an important reduction in manufacturing costs.

Analysis of hydrogen absorption during activation in powdered samples shows that the process is governed by the surface-related stages in untreated samples and by diffusion in the bulk in HF-treated samples. This means that, after the proposed surface treatment, hydrogen dissociation and pick-up on the surface is no longer the limiting stage during absorption.

After a few hydrogen absorption–desorption cycles at room temperature the treated samples attain their best performance for technological applications without requiring any special manipulation.

Acknowledgements

We wish to thank Hernán Peretti and Ernesto Aranda for the samples. This work was partially supported by Cooperativa de Electricidad Bariloche and ANPCyT PICT97-0000-00680.

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