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Activation characteristics of chemically treated $LaNi_{4.7}Al_{0.3}$

F.-J. Liu[1], G. Sandrock[2] and S. Suda*
Kogakuin University, Department of Chemical Engineering, Chemical Energy Laboratory, 2665-1, Nakano-machi, Hachioji-shi, Tokyo 192 (Japan)

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Abstract

The H_2 activation characteristics of the hydriding AB_5 intermetallic compound $LaNi_{4.7}Al_{0.3}$ were determined before and after chemical surface treatment in an F-containing aqueous solution (F-treatment). The F-treatment results in an Ni-rich surface which is overlaid by a net-like LaF_3 layer and results in a pronounced decrease in the time required for activation, as much as two orders of magnitude. The ease of activation is attributed mostly to the Ni-rich sublayer, although the LaF_3 overlayer may contribute to long term protection of the sublayers from deleterious gases such as air and H_2O vapor. Increasing the ease of activation will allow the use of thinner wall, lower cost containers for practical hydriding applications.

1. Introduction

It is well known that hydriding alloys must be *activated* in order to absorb H_2 the first time. This is a result of natural surface contamination from exposure to the air, usually in the form of oxides or hydroxides [1–5]. Activation usually consists of two stages. First, there is the initial penetration of the original contamination layer by H_2, at which time the molecular H_2 can be dissociated to atomic H on the metallic substrate before entering the bulk lattice. Second, there is the fragmentation of the alloy particles (decrepitation) resulting from the bulk absorption of hydrogen and the associated embrittlement and volume changes. The first stage is highly dependent on the original surface contamination and the second stage creates new clean surfaces. It is the first stage we address in this paper. Once the first stage is completed, the second stage usually takes care of itself if clean H_2 is used.

The original (air-exposed) surface can be a formidable barrier to H_2 penetration. For example, some Ti or Mg alloys must be heated under vacuum, inert gas or H_2 to dissolve or disrupt the oxide layer before any H_2 reaction can occur. The rare earth–nickel AB_5 compounds fortunately do not have to be heated, but unfortunately require substantial overpressures for activation to occur within reasonable times at room temperature. Thus, it is traditional to design the reaction vessel, not for the relatively modest pressures of normal cyclic use, but rather the abnormally high pressure required for *in situ* activation. If we can lower the pressures required for activation, then we can decrease the vessel wall thickness which has benefits to cost, weight, heat transfer, etc.

It is the purpose of this paper to present results of a powerful new approach for increasing the ease of activation of AB_5 hydriding alloys by chemically treating the original particle surfaces in an F-containing aqueous solution. For the purpose of brevity, we will call this proprietary Kogakuin process "F-treatment". This paper presents mostly data on H_2 activation improvements resulting from the F-treatment. Other papers discuss the resulting surface structures in more detail [6, 7].

2. Experimental details

The $LaNi_{4.7}Al_{0.3}$ used was produced commercially by vacuum induction melting. Most of the F-treating and activation studies were performed on 106–250 μm powder, although some powder in the range of 26–150 μm was used for microstructural observations. Freshly crushed powder and powder stored several months were compared, both in the untreated and F-treated conditions.

The F-treatment solution itself and process details cannot be disclosed in detail at this time because of impending patent filing activities. However, we can say

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[1] Visiting Researcher from Beijing General Research Institute for Non-ferrous Metals, Beijing, People's Republic of China.
[2] Special Visiting Research Scientist from SunaTech, Inc., Ringwood, NJ, USA.
*Author to whom correspondence should be addressed.

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that a special aqueous solution, containing active F^{-1} ions, is used for several hours at room temperature, followed by water washing and drying. The result of this F-treatment is a surface which contains active metallic Ni which is covered by a net-like layer of LaF_3. Untreated samples will hereinafter be designated UN and F-treated samples will be designated FT.

H_2 activation tests were run on standard Sieverts apparatus at 40 °C, usually using a starting pressure of about 10 atmospheres absolute. The pressure of 10 atmospheres was chosen for a very practical reason. For many countries (including Japan and the US), pressure vessel codes and requirements are much simpler if the pressures are kept below 10 atmospheres. In order to examine pressure effects, a few pressures other than 10 atm were tried. Evacuation time was constant for each specimen at 30 minutes and a vacuum of about 10^{-2} Torr.

Scanning electron microscopy (SEM) was performed on a Shimazu EPMA-8075 instrument. Some X-ray diffraction was tried but was not found to be sensitive enough to record peaks from the very thin (a few microns) surface structures.

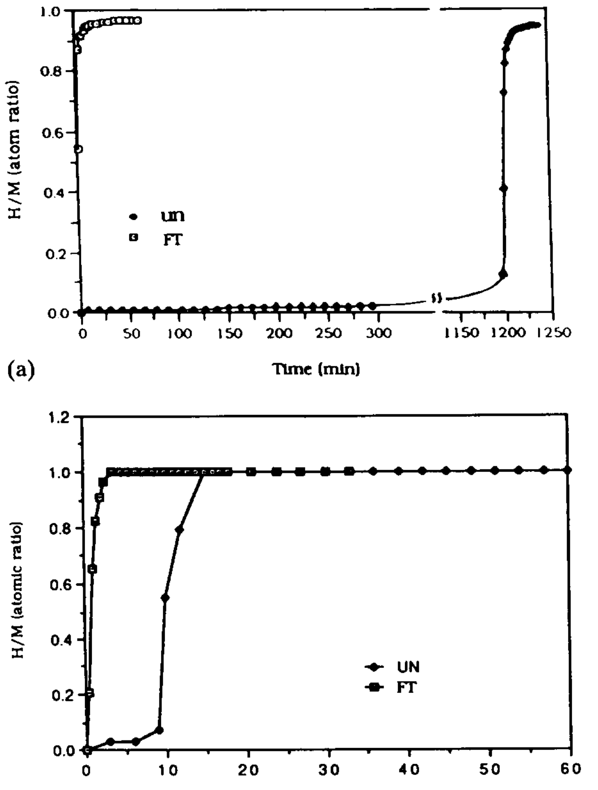

Fig. 1. Comparison of untreated (UN) and F-treated (FT) H_2 activation curves for $LaNi_{4.7}Al_{0.3}$ powder at 10 atmospheres pressure: (a) stored in air several months after crushing; (b) freshly crushed.

3. Results and discussions

The longer AB_5 compounds are stored after crushing, the harder they are to activate. As shown in Fig. 1, F-treatment eliminates this problem. Figure 1(a) shows UN and FT activation (first H_2 absorption) curves for $LaNi_{4.7}Al_{0.3}$ powder that was stored several months before treating. The untreated sample shown required an incubation time of nearly 20 hours. F-treatment virtually eliminated the incubation time with no loss of H_2-capacity. The effect of F-treatment is quite impressive on long-stored material. It is less impressive on freshly crushed materials, which have relatively short activation times anyway. As shown in Fig. 1(b), untreated, freshly crushed $LaNi_{4.7}Al_{0.3}$ activates in only about 10 minutes compared with 1200 minutes for the long-stored sample of Fig. 1(a). Even so, F-treatment can reduce this time further, down to a minute or so. In summary, however, the real benefit of F-treatment is for materials that have to be stored for long periods after crushing. In fact, significant storage time is the usual case for most practical purposes.

The effects of pressure on the activation of freshly crushed (few days' storage) powder, without and with F-treatment, are shown in Figs. 2(a) and 2(b), respectively. At all pressures, F-treatment reduces ac-

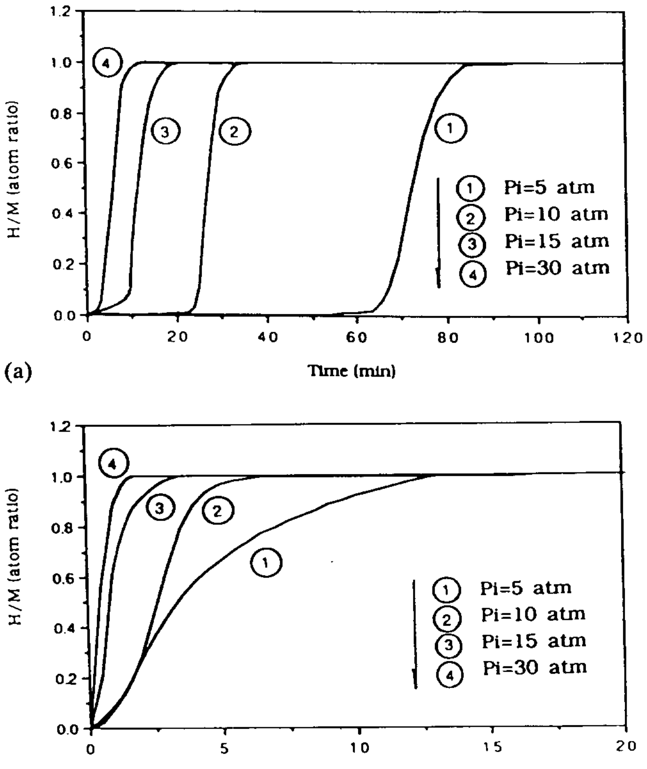

Fig. 2. Comparison of untreated and F-treated H_2 activation curves for $LaNi_{4.7}Al_{0.3}$ powder at various pressures: (a) untreated; (b) F-treated.

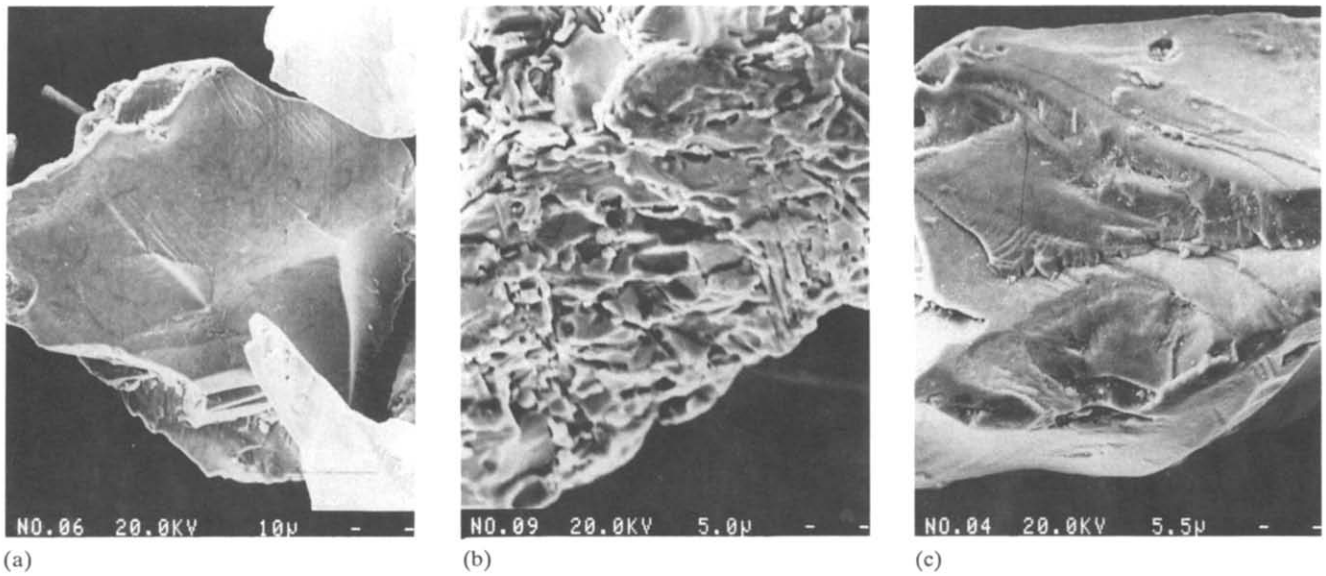

Fig. 3. SEM image of $LaNi_{4.7}Al_{0.3}$ powder particles: (a) untreated (as-crushed); (b) F-treated; (c) F-treated followed by ultrasonic cleaning for 2 hours in water.

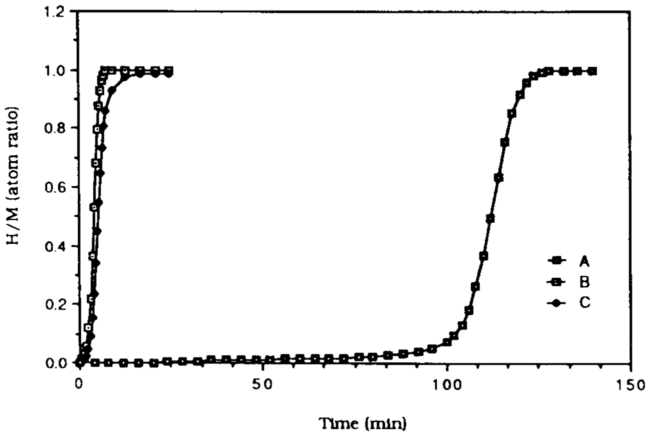

Fig. 4. H_2 activation curves for powder samples depicted in Fig. 3.

tivation time, largely by the elimination of the incubation period. A reasonable extrapolation of Fig. 2(b), representing FT samples of the subatmospheric plateau $LaNi_{4.7}Al_{0.3}$ intermetallic, suggests it may be possible to activate at atmospheric H_2 pressure. This may have some special practical implications for very thin wall containment and heat transfer.

The F-treatment process results in a net-like LaF_3 structure overlaying a metallic Ni-enriched layer. This structure is shown by SEM in Fig. 3(b). Note the rough fluoride surface in comparison with the smooth, relatively featureless untreated (as crushed) powder shown in Fig. 3(a). The net-like fluoride is relatively brittle and can be removed by ultrasonic cleaning in water, restoring a smooth substrate which contains relatively little fluoride but is enriched in Ni. In order to assess the relative roles of the net-like LaF_3 and its Ni-rich substrate, activation curves for the three samples shown in Fig. 3 were determined and are shown in Fig. 4. It can be clearly seen that the removal of the LaF_3 net-like structure does not adversely affect activation behavior of the treated material. This implies that it is principally the Ni-rich sublayer that is contributing most to improving the ease of activation. However, the LaF_3 overlayer is believed to give some long term shielding protection to the lower layers from deleterious gases such as air and H_2O vapor, although this is yet to be quantified.

4. Conclusions

The F-treatment process accomplishes the following when applied to $LaNi_{4.7}Al_{0.3}$ powder:

(1) It greatly decreases the H_2 activation time, especially on samples that are stored for significant periods of time after crushing. In the case of samples stored for a few months, the reduction in activation times can be two orders of magnitude.

(2) Activation times are reduced by F-treatment for all applied H_2 pressures.

(3) The ability to activate in reasonable time periods at lower pressure will allow the use of thin wall containers designed more closely to the moderate cycle pressures rather than the high *in situ* activation pressures used in the past.

(4) The improved activation properties are mainly a result of the formation of an Ni-rich sublayer during F-treating. An overlying net-like LaF_3 layer may provide

some protective shielding to the lower layers from deleterious gases such as air and H_2O vapor.

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