ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 632–635

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Pulverization behavior of $LaNi_5$ with alkaline pretreatment

Yuka Ozu[a], Toshiro Kuji[b], Haru-Hisa Uchida[a,*]

[a]*Department of Human Development, Tokai University, Kitakaname 1117, Hiratsuka, Kanagawa, 259-1292 Japan*
[b]*Corporate R&D Center, Mitsui Mining and Smelting Co. Ltd., 1333-2 Haraichi, Ageo, Saitama, 362-0021, Japan*

Abstract

Surface pretreatment on $LaNi_5$ powder sample using LiOH accelerates the H_2 absorption even after significant oxidation. In this paper, pulverization of pretreated powder sample was investigated. In the case of the smaller initial grain size, the faster pulverization is proceeded. The consideration of surface area, including generated surface during the cycling indicates that only the initial surface with LiOH treated seems to be active to H_2 after significant oxidation. Additionally we propose a new presentation method for the powder distribution including information on particle forms.

Keywords: $LaNi_5$; Alkaline pretreatment; Pulverization behavior

---

1. Introduction

In the hydrogen absorption reaction, the surface condition is a predominant factor especially for the initial reaction rate, where the surface oxide layer not only prevents the dissociative hydrogen absorption, but also affects on the pulverization [1]. Additionally, in the activation process of hydrogen storage alloys, the prior alkaline treatment drastically enhances the initiation of dissociative absorption [2]. In Ni–H batteries, charge–discharge characteristic can be also significantly improved by the pretreatment with alkaline hydroxides, such as sample boiling in the KOH solution [3]. Recently we reported the effect of LiOH pretreatment on the H_2 absorption kinetics with air oxidation [2], which describes that the LiOH pretreatment enhances H_2 absorption even after several significant air oxidations.

In this study we investigated, therefore, the effect of LiOH pretreatment on pulverization of $LaNi_5$, because the pulverization depends on the surface conditions [1].

Additionally we propose a new presentation method for indicating the powder distribution including information of particle forms, while the manner of usual histograms for the particle distribution cannot indicate the forms and shapes of grain particles.

2. Experiment

The sample $LaNi_5$ was prepared by arc melting process and subsequent annealing for the homogenization. The block sample was pulverized for 15 times 40 bar H_2 sorption cycles using a high-pressure volumetric apparatus and placed under dry air for longer than 1 month before use. The sample powder was put through a sieve (45 μm) and divided into two groups of grain sizes as large (over 45 μm) and small (under 45 μm) powder samples. Some sample powder was placed in 3 M-LiOH solutions for 2 h without any subsequent water washing and dried at room temperature under atmosphere. After 30 cycles of absorption (5 min) and desorption (5 min) using 7 N-H_2 (99.99999% purity), the particle size was observed by using scanning electron microscope (SEM) for more than 200 sample particles. The lengths in short and long axes of each particle were measured and plotted. Averaged value was used for the histograms.

Because in the manner of usual histograms the particle distribution could not indicate the forms and shapes of grain particles, a new presentation method for the powder

---

*Corresponding author. Fax: +81-463-502208.
E-mail address: hhuchida@keyaki.cc.u-tokai.ac.jp (H.-H. Uchida).

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01666-8

distribution including information of particle forms was additionally examined. This manner was also applied for the powder sample of $LaNi_{2.5}Co_{2.5}$, which is known as less pulverized by the sorption cycles [4].

3. Results and discussion

The histograms of the particle size of $LaNi_5$ after 30 cycles with and without initial LiOH treatment and SEM micrograph of particles are shown in Figs. 1 and 2, respectively. Although the conventional histogram shows only averages of grain particle sizes, the particles are not in uniform as shown in Fig. 2. We take, therefore, different presentation method to show the size distribution including information of particle forms as shown in Figs. 3 and 4, where the lengths in short and long axes of more than 200 particles are plotted. The characteristics of particle form can be presented in the figure, where more rectangular particles are plotted downwards; the dot line of 1/4 or 1/2 means the ratio of short and long axes.

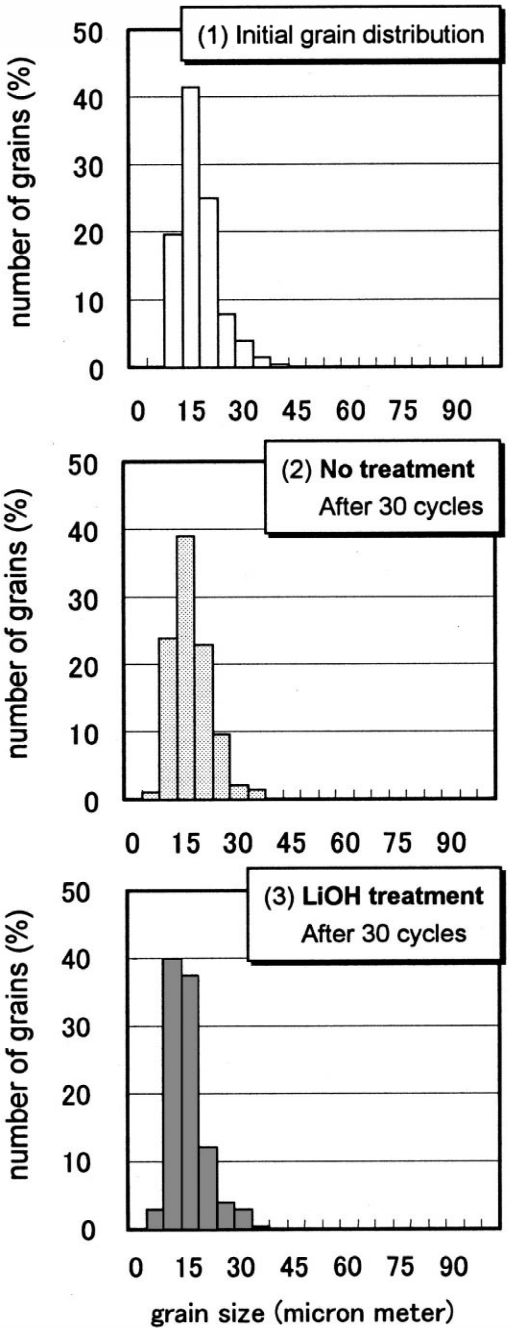

Fig. 1. Histogram of the particle size of $LaNi_5$ with and without LiOH pretreatment with the initial size of under 45-μm.

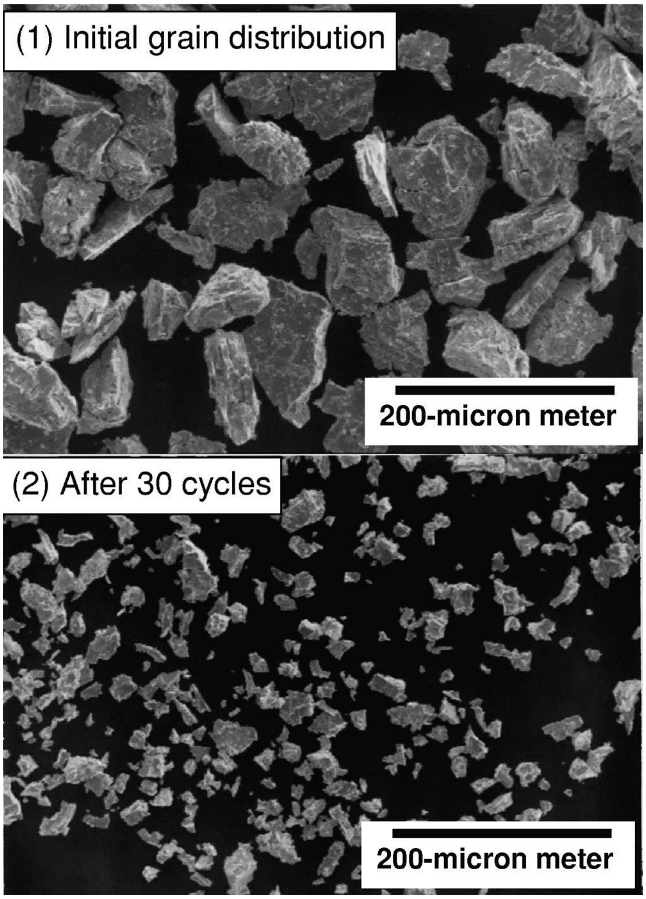

Fig. 2. Scanning electron micrograph of the $LaNi_5$ before and after 30 cycles H_2 absorption.

Fig. 3 shows the distribution of the pulverization of $LaNi_5$ with and without LiOH pretreatment for both larger and smaller initial grain size samples. After 30 cycles the pulverization is accelerated with LiOH pretreatment, if the initial grain size is smaller than 45 μm. On the other hand, for the samples with larger initial grain sizes (>45 μm), almost no difference is observed in the pulverization (see Fig. 3B, (2) and (3)). The enhanced pulverization is generally considered to be the crack initiations attributed to dislocation stacking at the metal–oxide boundaries, which is yielded by the volume expansion in the course of H_2 absorption [1]. Similar mechanism may also be considered for the sample with LiOH treatment, where the cracks are

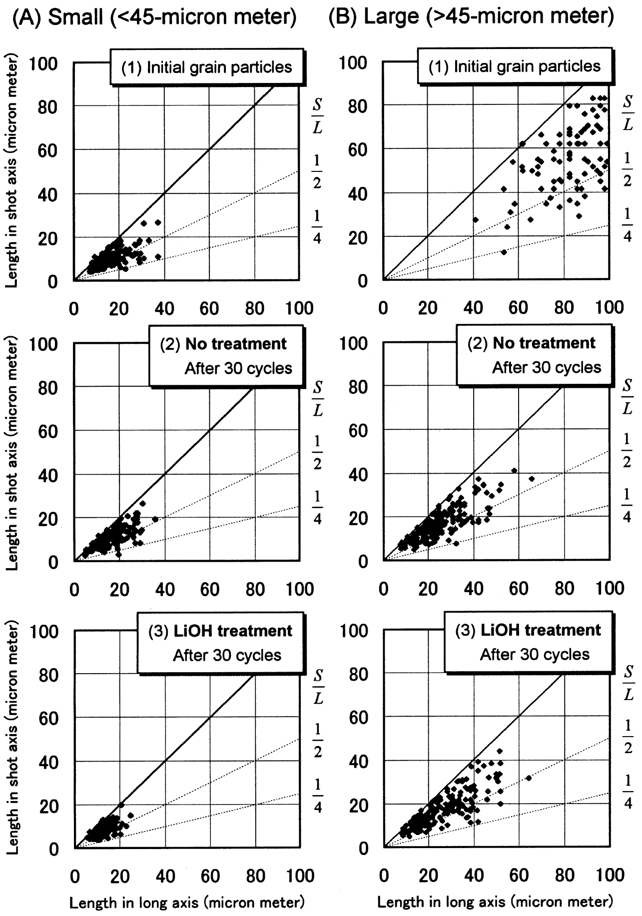

Fig. 3. Powder size distributions of $LaNi_5$ with and without LiOH pretreatment for smaller and larger initial grain sizes.

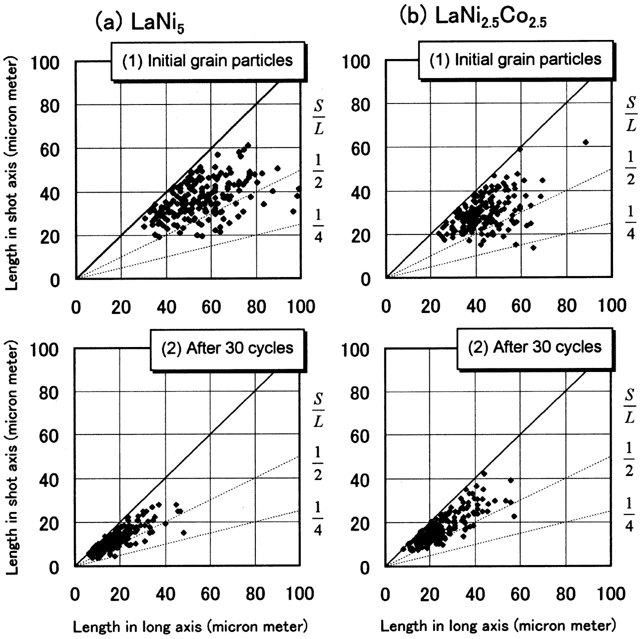

Fig. 4. Powder size distributions of: (a) $LaNi_5$ and (b) $LaNi_{2.5}Co_{2.5}$ without LiOH pretreatment.

initiated at the modified metal–oxide surface by the LiOH treatment. The smaller particle with larger initial surface area seems to exhibit the effects more predominantly.

Fig. 4 shows the results of pulverizing characteristics of $LaNi_{2.5}Co_{2.5}$ without LiOH treatment. The addition of Co to La–Ni alloy is known to restrain the pulverization because of the smaller volume expansion [4]. As shown in Fig. 4 the sample $LaNi_{2.5}Co_{2.5}$ is less pulverized than that of $LaNi_5$ after 30 cycles. Additionally, $LaNi_5$ maintains similar particle forms, while the grains of $LaNi_{2.5}Co_{2.5}$ are becoming more homogeneous form, i.e. rectangular form particles decrease with increasing the cycle number.

The effect of LiOH on the pulverization of $LaNi_{2.5}Co_{2.5}$ was not observed distinctly after 30 sorption cycles. The addition of Co restrains pulverization also for the sample with LiOH treatment.

The pulverization behavior affects also drastically on the reaction kinetics. Fig. 5 shows the H_2 absorption kinetics of $LaNi_5$ with and without LiOH pretreatment [2]. Before H_2 sorption measurements, the sample was exposed to air for 5 min at the first oxidation and two times of 5-min (total 10 min) air exposures at the second oxidation. Subsequent oxidations until five times of 5 min air oxidations were carried out. As shown in Fig. 5 the existence of Li in the surface oxide layer seems to accelerate the H_2 dissociation or H penetration through the oxide layer. Increasing the amount of oxidation, however, decreases the initial absorption rate even the sample is treated by LiOH. Because the initial reaction rate depends

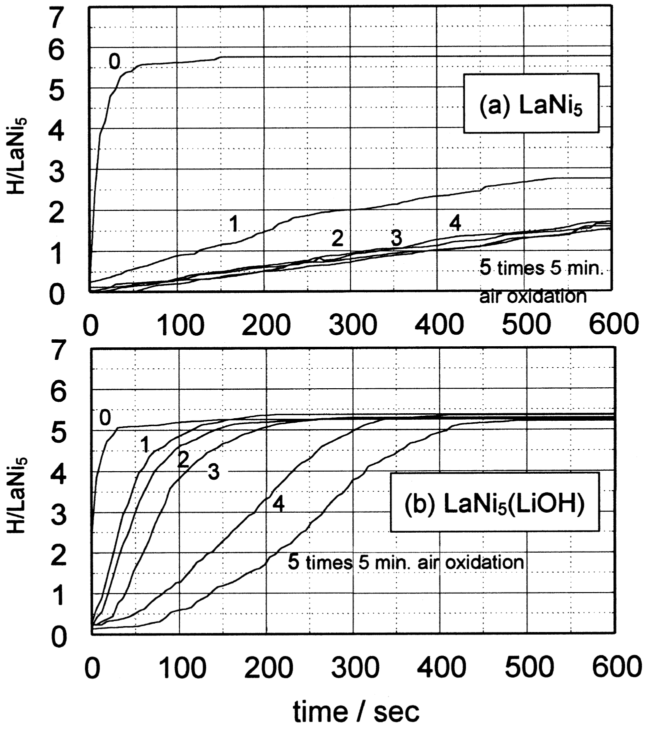

Fig. 5. Hydrogen absorption of $LaNi_5$ (initial pressure of 40 bar H_2) with increasing amount of air oxidation, (a) without and (b) with LiOH pretreatment.

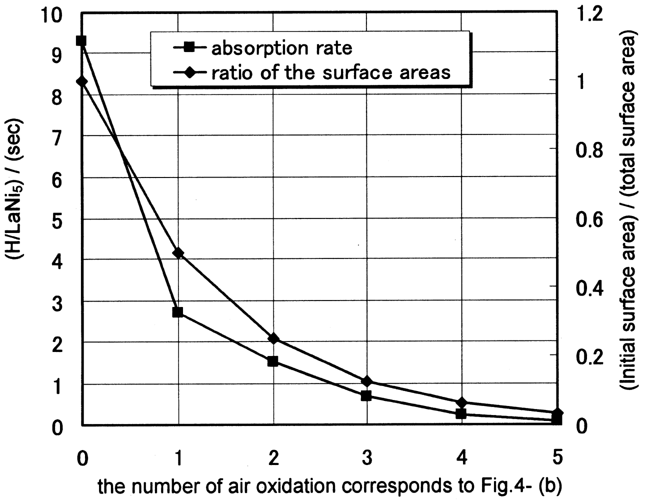

Fig. 6. Comparison of initial absorption rate and the ratio of initial surface area to the total surface area with the number of air oxidations (see Fig. 5). The surface area was considered to increase to double area at each absorption after the oxidation.

on the surface area and the surface condition, we consider the following models.

The ratio of initial surface area treated with LiOH to the total surface area for each cycle number can be considered according to a simple pulverization model, where one particle is pulverized into several smaller particles with double surface area by each sorption cycle. Fig. 6 shows the initial absorption rate of the H_2 absorptions shown in Fig. 5 and the surface area ratio at each number of oxidations. Both the sorption rate and the surface ratio decrease with increasing number of oxidation. This consideration results in a reasonable sorption mechanism that the H_2 absorption occurs only on the surface with LiOH pretreatment, which decreases relatively with the subsequent sorption cycles. The decelerated absorption rate by the air oxidation (Fig. 4) can be explained by the decrease of relative initial surface area with LiOH treatment, while the generated clean surface by the pulverization deactivated by the oxidation.

4. Conclusion

In this study the effect of LiOH pretreatment on pulverization of $LaNi_5$ and $LaNi_{2.5}Co_{2.5}$ was investigated. The pulverization of $LaNi_5$ is accelerated for the sample with smaller initial grain sizes. However, almost no difference is observed for the sample with larger initial grains. This difference indicates that the surface layer pretreated with LiOH enhances the pulverization like the surface of the oxide layer. In the case of $LaNi_{2.5}Co_{2.5}$ no accelerated pulverization was observed for the sample with and without the treatment.

Decreasing the initial sorption rate with increasing amount of air oxidation shown in Fig. 5 is attributed to the decrease of the ratio of initial surface area treated with LiOH to the total surface area at each sorption cycle, where the new surface generated by the pulverization is deactivated by air oxidation. If one particle is pulverized to adequate number of smaller particles with double surface area at each absorption, the degradation of the reaction kinetics by oxidations can be well explained.

Larger initial surface area with LiOH treatment is preferred for the H_2 absorption including oxidations, while pulverization is proceeded if the sample particle sizes are smaller. Adequate sizes may exist for both the accelerated reactivity and restrained pulverization. Further investigations are necessary also for pulverization at a higher number of cycles.

In this paper, we propose a new presentation manner for indicating the powder distribution including information of particle forms. This plot manner may be also applied to the other sample powders.

Acknowledgements

This study was carried out in a frame of Eco-Technology Project of Tokai University.

References

[1] H. Uchida, N.H. Uchida, Y.C. Huang, J. Less-Common Met. 101 (1984) 459.
[2] H.H. Uchida, Y. Ozu, K. Suzuki, S. Kubo, A. Yoshizawa, J. Alloys Comp. 293 (1999) 369.
[3] H.H. Uchida, Y. Watanabe, Y. Matsumura, H. Uchida, J. Alloys Comp. 231 (1995) 679.
[4] J.J.G. Wilems, K.H.J. Buschow, J. Less-Common Met. 129 (1987) 13.