

The Effect of the Surface Condition on the Incubation Time of $\text{LaNi}_{4.7}\text{Al}_{0.3}$

Jeong-Seb Han*, Wang Xianglong** and Seijirau Suda**

*Department of Ocean Engineering, Dong-A University
840 Hadan-Dong, Saha-gu, Pusan, Korea

**Department of Chemical Engineering, Kogakuin University,
Nakano-machi 2665-1, Hachioji-shi, Tokyo 192, Japan

요약 : 표면상태가 $\text{LaNi}_{4.7}\text{Al}_{0.3}$ 의 활성화에 미치는 영향을 조사하기 위해서 여러가지 산화 상태에서의 incubation time 을 관찰하였다. Incubation time은 입자의 크기, 파쇄후 경과시간, 합금방법에 따라 다르게 나타났다. 재료를 파쇄한후 실험한 날짜에 따라 incubation time은 초기에는 증가하다가 최대점을 지난후 감소하고 다시 최소점을 보인후 증가하는 현상을 보였다. 이것은 Ni cluster와 산화층의 복합적인 작용인 것으로 생각된다. Ni cluster의 양과 산화층의 두께는 공기에 노출되는 시간이 증가함에 따라 증가하였다.

1. Introduction

The activation process of the hydrogenation of metals is of importance relative to their practical use as hydrogen storage materials. The activation of LaNi_5 system is easier compared to many other hydrogen storage materials, such as TiFe , Mg_2Ni etc.. But it needs many absorption and desorption cycles for activation although it does not need heat treatment. That is ascribed to the state of the surface. The surface state is different according to the particle size, pretreatment, manufactural procedures, surface morphology and etc.. The surface of LaNi_5 system exposed to air is covered with stable

oxides and hydroxides of the alloy¹⁻³⁾. These oxides layer can be easily formed at room temperature. These markedly prohibit the absorption of hydrogen. Especially the 1st absorption rate in the activation process strongly depends on the kinds of oxides in the surface.

Up to now, there is few study to investigate in detail about the effect of air exposure on the activation although the partial examinations were undertaken⁴⁻⁶⁾. In this paper attempts are made to investigate the effect of surface state on the activation by observing the incubation time of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ at various oxidation conditions.

2. Experiment

A $\text{LaNi}_{4.7}\text{Al}_{0.3}$ ingot was made by induction melting at Japan Chuo Denky Co.. The ingot was crushed into powder. After sieving, all the samples were inputed to sample bottles, which have tightly close caps. By these caps the rate of oxidation of sample was controlled. The rate is belived to be more slower than fully air exposure. In this case the various experiments can be performed at many different surface conditions. Three kinds of particle sizes were used. a) large size(between 0.106 and 0.250mm), b) medium size(between 0.075 and 0.106mm), and c) small size(under 0.075mm). Sample of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ of 2g was used in a Sievert type of apparatus. To remove heat effect a double wall reactor was used. The thickness of sample bed was kept within 0.7mm between outer and inner tube. The shape was described in ref. 7. All the samples were reacted at 50°C under 110 kPa of hydrogen. The pressure changes were measured by an strain gauge type pressure transducer. All the data were stored in the Hewlett-Packard 3052A data acquisition system. To measure by ESCA and SIMS, the lumps of samples were cutted with diamond cutter and then were grinded until mirror planes were appeared. ESCA and SIMS measurements were carried out on a ESCA-850M analyzer(Shimazu). Base pressure in the spectrometer was at 10^{-7} Pa, and Mg K_{α} ($h\nu = 1253.6$ eV) radiation was used.

3. Results and Discussion

3.1 Incubation time of $\text{LaNi}_{4.7}\text{Al}_{0.3}$

Han and Lee⁸⁾ have reported that up to $H/M = 0.4 - 0.5$ the dissociation chemisorption of hydrogen molecules on the sample surface is the rate controlling step of hydrogen absorption by $\text{LaNi}_{4.7}\text{Al}_{0.3}$. Wang and Suda⁹⁾ also suggested that the surface process is a possible rate controlling step in the α

phase of $\text{LaNi}_{4.7}\text{Al}_{0.3}$. Above mentioned results were obtained by the kinetic study with activated sample. In case of unactivated sample like this attempts, surface reaction should be rate controlling step. Therefore 1st absorption rate strongly depends on the surface state.

Fig. 1 shows typical results of 1st absorption rate of $\text{LaNi}_{4.7}\text{Al}_{0.3}$. The absorption rates are very slow initially and then increase rapidly. The initial period is termed as the incubation time. The incubation time is thought to be the time required for the hydrogen molecular dissociation and for the hydrogen penetration into the surface to be hydrogenated. After incubation time the hydride will be formed

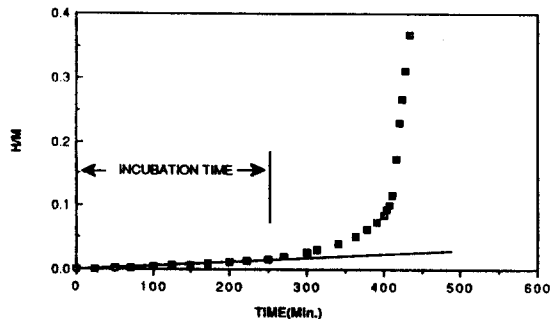


Fig. 1. The definition of incubation time.

and crack formation occurred. After crack formation new surface uncontaminated is formed. This new surface might be a factor for rapid absorption. Fig. 2, 3, 4 show 1st absorption rate measured for various surface conditions of $\text{LaNi}_{4.7}\text{Al}_{0.3}$. All the results show same trends in the behavior of incubation time. The trend can be obviously seen through Fig. 5. In Fig. 5 only incubation time of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ is plotted using Fig. 2, 3, 4. The trend is composed of 3 stages. After crushing of sample, the experiment was carried out with different elapse time. The incubation time becomes first longer. We call it A stage. And then it becomes shorter. We call it B stage. Finally it becomes longer again. We call it C stage. In our knowledge, for the first time

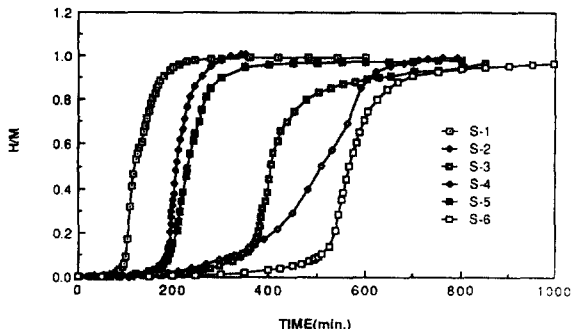


Fig. 2. The various incubation time measured for different days after crushing with small particle size(S-1 ; 1.0 day, S-2 ; 5.0, S-3 ; 7.9, S-4 ; 11.9, S-5 ; 15.9, S-6 ; 20.8).

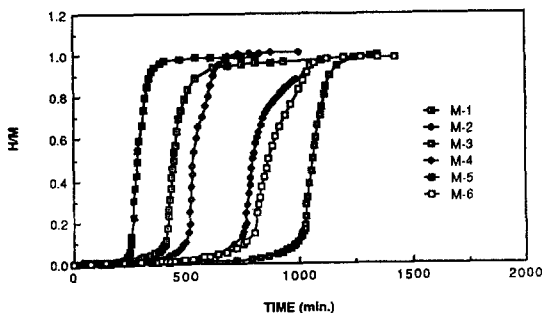


Fig. 3. The various incubation time measured for different days after crushing with medium particle size(M-1 ; 1.9 day, M-2 ; 5.3, M-3 ; 9.3 M-4 ; 12.8, M-5 ; 17.8, M-6 ; 21.8).

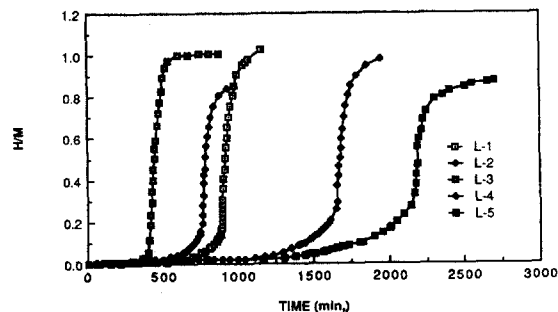


Fig. 4. The various incubation time measured for different days after crushing with large particle size(L-1 ; 3.2 day, L-2 ; 6.1, L-3 ; 10.8, L-4 ; 14.9, L-5 ; 18.9).

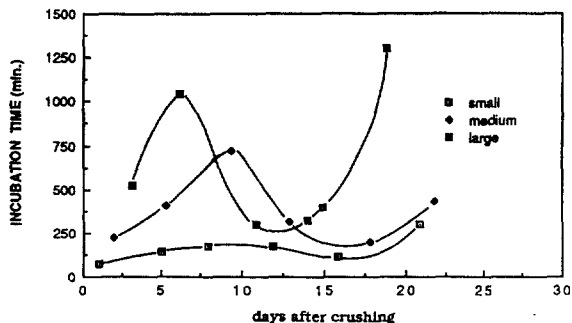


Fig. 5. The various incubation time of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ according to particle size.

these behaviours are observed. The published results^{4,6)} showed that after crushing of sample the incubation time becomes only longer with different elapse time. The reason is considered to be that they exposed the samples to the air fully or their experimental period was too short. If the sample is exposed to the air fully, the B stage can not be observed because the oxidation rate is very fast.

In the A stage the larger the particle size, the steeper the slope. The slope is to be considered as the rate of the contamination of active sites per unit surface area. In this stage the clean $\text{LaNi}_{4.7}\text{Al}_{0.3}$ is assumed as active site. The contamination means a process before the perfect separation of the $\text{LaNi}_{4.7}\text{Al}_{0.3}$ to La_2O_3 and Ni. And contaminated active site will be inactive. The amount of oxygen supplied was almost same by the cap of the sample bottle. Because the large particles have less total surface area, the rate of contamination of active site per unit surface area is fastest than others. Namely the incubation time is longer. And if there is no cap, fully air exposure, because the rate of the supply of oxygen is very fast, all the slopes will be very steep. If the activity of surface site is different the slope also will be changed although the particle size is same. To investigate the effect of the activity of surface site, a sample which was made by the arc melting was tested. The result is shown as Fig. 6.

The A stage can not be seen because the slope of A stage is very steep.

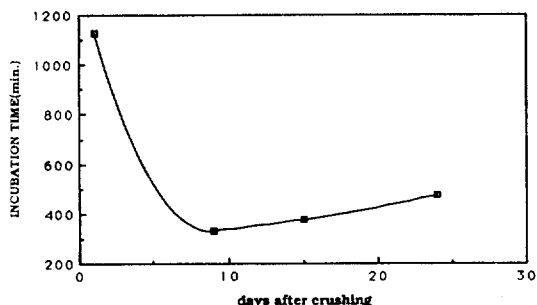


Fig. 6. The incubation time of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ made by means of arc melting.

As shown as Fig. 5, as the particle size is increased, the maximum point of incubation time is increased, namely 240, 700, 1000 min. This is maybe caused by the difference of the density and the defects of oxides layer due to the initial curvature of the particle surface¹⁰). As the size of particle is decreased, there is a possibility of easy penetration of hydrogen through oxides having less density and many defects.

The second stage is considered as the effect of the metallic Ni. In the surface region of the particle, La atoms diffuse to the surface and oxidized prior to Ni atoms. The amount of metallic Ni becomes larger. It is well known that metallic Ni facilitates the dissociative hydrogen chemisorption¹¹). Therefore the incubation time becomes shorter. This will be more explained at next section, 'composition of surface'.

At the third stage, La continually diffuses to the surface and is oxidized. The remained Ni atoms are much more covered by the lanthanum oxides. The layer of surface oxides becomes thicker. Therefore the dissociation of hydrogen molecules and the permeation of hydrogen atom through the layer are very difficult. That means incubation time becomes longer.

In this experimental condition, up to 8 days after crushing small particle has shortest incubation time. The large particle has longest incubation time. However between 9 day and 13 day after crushing of sample, the sequence is changed. Small particle has the shortest incubation time. And medium particle has the longest incubation time. After 14 day once more the sequence is changed. These sequence will be changed according to experimental conditions. Therefore to compare first absorption rate with particle size experimental condition should be carefully controlled. The rate of contamination should be same and the experiment had better be done simultaneously and the experimental date after crushing is also important. According to experimental date (ex, between 8–13 days), even if the rate of contamination is same and the experiment is carried out simultaneously, the result will be changed.

3.2 Composition of the surface

The surface composition was determined by the means of XPS for the $\text{LaNi}_{4.7}\text{Al}_{0.3}$ alloy after exposing in air for 1, 15 and 30 days. The spectra for the La $3d_{5/2}$, Ni $2p_{1/2}$ and Al $2p$ levels were determined. La bond on the surface was recognized as La_2O_3 with a small amounts of $\text{La}(\text{OH})_3$. Metallic La ($E_b=836$ eV) existed at the sublayer. Ni $2p_{1/2}$ core level was used to identify the chemical state. It was observed that Ni existed in the metallic state ($E_b=870$ eV). Al existed in the form of Al_2O_3 ($E_b=73.7$ eV) on the top surface and metallic Al ($E_b=72.0$ eV) appeared after etching for 2–4 minutes.

Segregation of elements for different exposure times was examined by Ar^+ sputtering. The depth profiles of metallic La to oxidized La are shown in Fig. 7 and the depth profiles of Ni to La (metallic and oxidized La) are shown in Fig. 8. It was observed that the ratio of metallic La to oxidized La decreased with the increase of exposure time. Especially, metallic La could not be observed on the surface

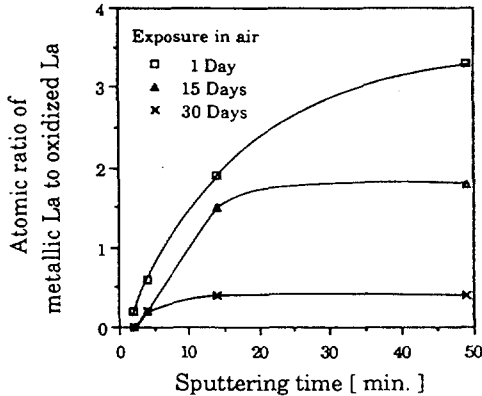


Fig. 7. An XPS depth profile of metallic La to oxidized La for the air exposed $\text{LaNi}_{4.7}\text{Al}_{0.3}$ alloy.

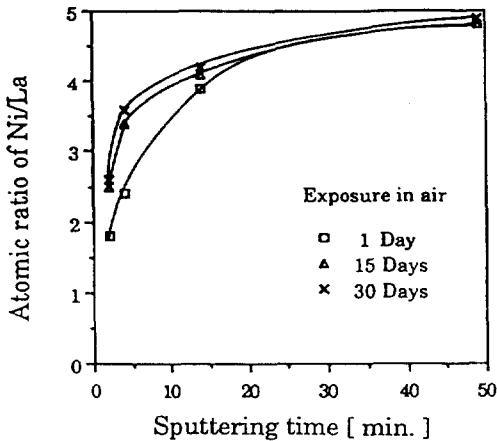


Fig. 8. An XPS depth profile of Ni to La (metallic and oxidized La) for the air exposed $\text{LaNi}_{4.7}\text{Al}_{0.3}$ alloy.

after sputtering for 2 min. for the alloy exposed in air for long time (15 and 30 days). This indicates that the thickness of the La oxide layer increases with increasing exposure time. From Fig. 8 it can be seen that the Ni was segregated from alloy face and precipitated on the sublayer during the La was oxidized. The amount of segregated Ni was increased with the increase of exposure time. The increment

of segregated Ni showed an abrupt change from 1 day to 15 days, but it changed slowly after exposing for long time. This indicates that the speed of oxidation was faster for the first few days and then slowed down after a thick layer of La oxide was formed.

Through the above observation, it is understood that by exposing the alloy to air, segregation of alloy components takes place on the surface. La_2O_3 layer is formed, and metallic Ni dissociates from the alloy phase and precipitates on the sublayer. The change of incubation time might be caused by the change of surface state and composition with increasing the exposure time in air. The newly crushed alloy has an uncontaminated surface which allows the hydrogen absorption proceed fast. With the increasing of exposing time, the metallic Ni dissociates from $\text{LaNi}_{4.7}\text{Al}_{0.3}$ phase and precipitates on the sublayer. This metallic Ni might play an important role for promoting a rapid hydrogen uptake during initial activation procedure by acting as an $\text{H}_2 \rightarrow 2\text{H}$ dissociation catalyst. Thus the hydriding reaction rate is promoted and the incubation time is reduced. But, after crossing the minimum point of incubation, the thickness of La oxide becomes thicker and thicker with increasing the exposure time. Thus hydrogen penetration into the new surface becomes more difficult although metallic Ni exists in the sublayer. This explains why the incubation time is reduced and then increased again.

Therefore The minimum point of incubation time can be explained by the mixed reaction of the effect of Ni cluster and the effect of oxide layer as shown in Fig. 9.

4. Conclusion

The Incubation time is different according to alloying method, particle size and experimental date after crushing of sample. The incubation time is increased and then reduced and finally increased

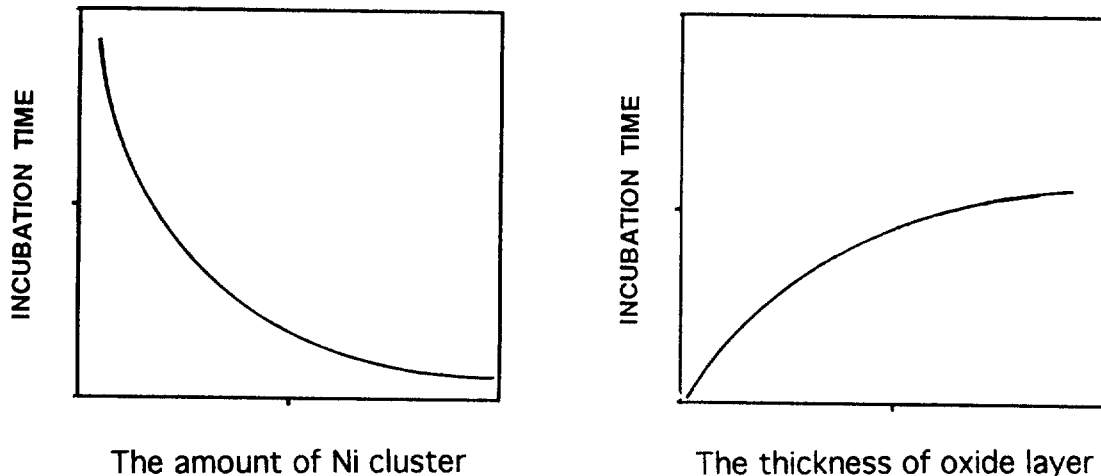


Fig. 9. The dependence of the incubation time on the amount of Ni cluster and thickness of oxide layer.

again with increasing the exposure time. There are maximum and minimum point in the incubation time. The point is changed with alloying method and particle size. The minimum point of incubation time is explained by the mixed result of the effect of Ni cluster and that of oxide layer. The amount of Ni cluster and the thickness of the La oxide layer increases with increasing exposure time.

References

1. P. Selvam, B. Viswanathan, C.S. Swamy and V. Srinivasan, *Int. J. Hydrogen energy*, Vol.16, No.1, 23(1991).
2. J. H. Weaver, A. Franciosi, W.E. Wallace and H. K. Smith, *J. Appl. Phys.*, 51, 5847 (1980).
3. L. Schlapbach, A. Seiler, F. Stucki and H. C. Siegmann, *J. Less-Common Met.*, 73, 145(1980).
4. H. Uchida and M. Ozawa, *Z. Phys. Chem. N.F.*, 147, 77(1986).
5. Y. Ohtani, S. Hashimoto and H. Uchida, *J. Less-Common Met.*, 172-174, 841(1991).
6. Jai-Young Lee, C.N. Park and S.M. Pyun, *J. Less-Common Met.*, 89, 163(1983).
7. S. Suda, N. Kobayashi and K. Yoshida, *J. of Less-Common Met.*, 73, 119(1980).
8. J.I. Han and J.Y. Lee, *Int. J. Hydrogen Energy*, Vol.14, No. 3, 181(1989).
9. X.L. Wang and S. Suda, *J. of Less-Common. Met.*, 159, 109(1990).
10. A.E. Evans and R.H. Cannon, *Proc. of the Norman L. Peterson Memorial symposium on "Oxidation of Metals and Associated Mass Transport"*, Orlando, USA, 135(1986).
11. H.C. Siegmann and L. Schlapbach, *Phys. Rev. Lett.*, 40, (14), 972(1978).