Journal of Alloys and Compounds, 194 (1993) 73–76
JALCOM 533

Surface study of chemically treated $LaNi_{4.7}Al_{0.3}$ alloy

X.-L. Wang and S. Suda
Department of Chemical Engineering, Kogakuin University, 2665-1, Nakano-machi, Hachioji-shi, 192 Tokyo (Japan)

(Received June 22, 1992; in final form September 23, 1992)

Abstract

Hydride-forming alloys with highly reactive surfaces have been developed by treating with a fluorine-containing aqueous solution. They exhibit excellent reactivity for hydrogen uptake. The surface properties of the fluorine-treated $LaNi_{4.7}Al_{0.3}$ alloy were studied by X-ray photoelectron spectroscopy and secondary ion mass spectroscopy. Surface compositions were analysed and compared with that of the untreated sample. After fluorine treatment, fine net-like crystallites of less than 1 μm are formed and segregation of the alloy components takes place on the surface.

1. Introduction

Hydrogen storage alloys generally require tedious activation procedures in order to obtain stable hydriding properties. This sometimes requires evacuation on heating and repeated hydriding–dehydriding cycles under relatively high pressure conditions. As the surface reactivity is governed by surface conditions, the activation procedure is more difficult after the sample has been exposed to the air for a long time (especially samples of smaller particle size with larger specific surface area) due to the formation of stable oxides and hydroxides [1, 2].

A fluorine (F) treatment method has been developed [3] in order to ease activation. The method involves the treatment of hydride-forming alloy particles with an F-containing aqueous solution to form surfaces with high hydrogen affinity and protection from impurities. The treated alloys exhibit excellent reactivity to hydrogen uptake [4].

The aim of this study was to analyse the surface properties of the F-treated alloy in order to evaluate the reasons for the improved H_2 activation. The surface compositions of chemically treated $LaNi_{4.7}Al_{0.3}$ were determined by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). The surface structure was determined by scanning electron microscopy (SEM). The results are compared with the untreated sample.

2. Experimental details

The sample was polished to ensure a flat surface and was then placed in a stirred F-containing aqueous solution at room temperature for several hours. As the patent is pending, details of the solution itself cannot be disclosed at this time. However, a special aqueous solution containing F^- ion was used. The treated sample was flushed several times with tap water and dried in air.

XPS and SIMS measurements were carried out on an ESCA-850M spectrometer (Shimadzu). The base pressure in the spectrometer was 10^{-7} Pa, and Mg Kα ($h\nu \approx 1253.6$ eV) radiation was used.

3. Results and discussion

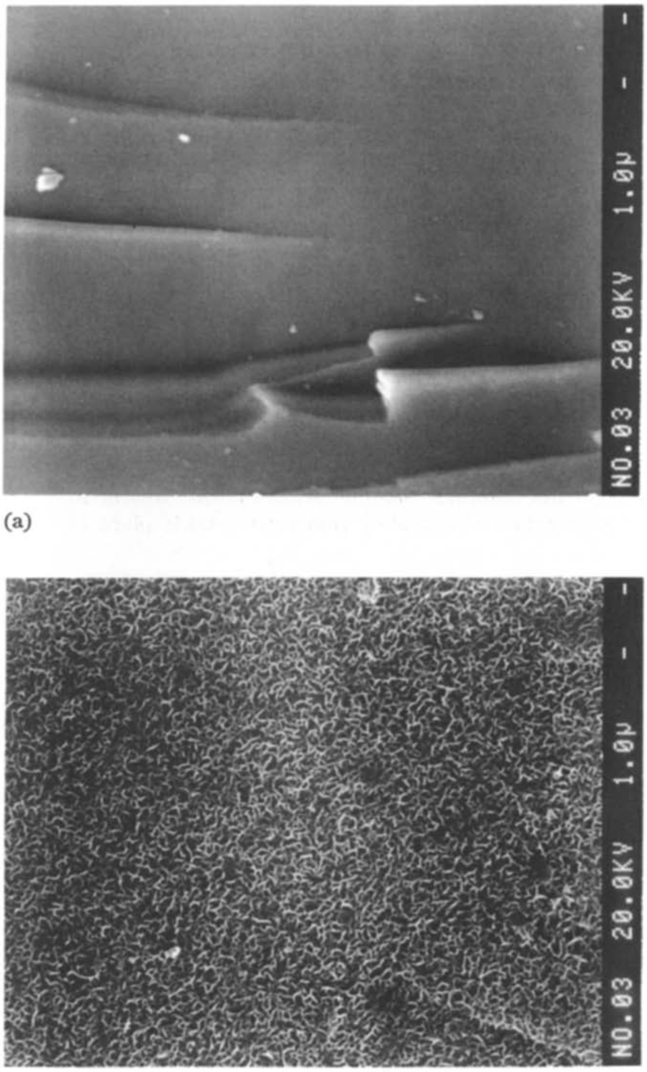
3.1. Morphology of the surface

The morphology of the untreated and treated $LaNi_{4.7}Al_{0.3}$ was viewed by SEM. Figure 1 illustrates the scanning electron micrographs of the untreated and treated surfaces. It can be seen that the untreated alloy exhibits a very smooth surface. However, very fine net-like crystallites of less than 1 μm were observed on the surface of the F-treated alloy. The specific surface area was determined as 0.026 $m^2\ g^{-1}$ for the untreated particles and 0.293 $m^2\ g^{-1}$ for the F-treated particles (particle size distribution, 0.250–0.106 mm). This indicates that the structure formed increases the specific surface area because of many fine channels.

3.2. Composition of the surface

X-Ray photoelectron spectra for the La $3d_{5/2}$, Ni $2p_{1/2}$ and Al 2p levels of the untreated sample are shown in Fig. 2 as a function of sputtering time. The La $3d_{5/2}$ core level spectrum splits into two species and

0925-8388/93/$6.00



(a)

(b)

Fig. 1. SEM observations of untreated (a) and F-treated (b) $LaNi_{4.7}Al_{0.3}$ surfaces.

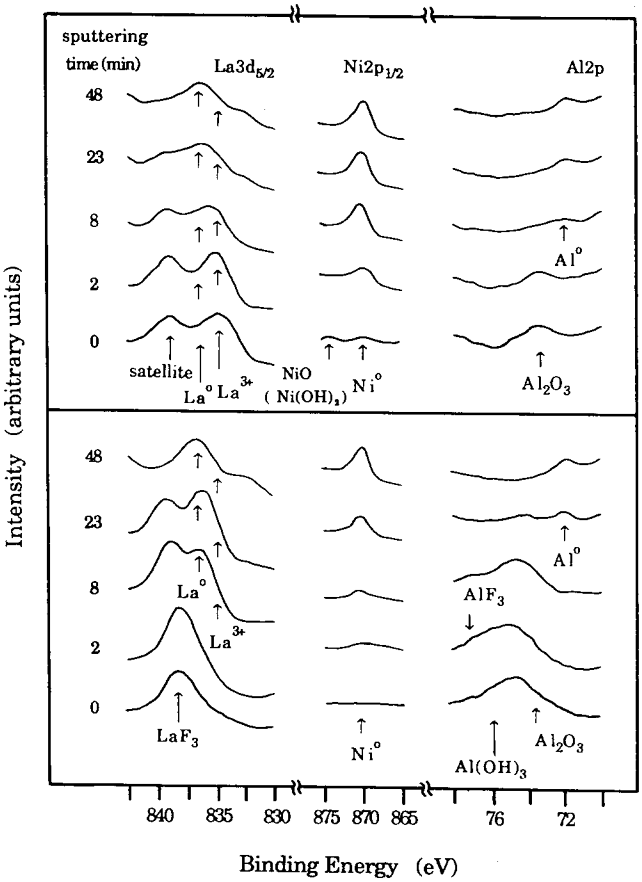


Fig. 2. X-Ray photoelectron spectra of the La $3d_{5/2}$, Ni $2p_{1/2}$ and Al 2p levels for F-treated and untreated $LaNi_{4.7}Al_{0.3}$ alloy: upper part, untreated surface; lower part, F-treated surface.

the separation energy is 4.0 eV. From the separation energy and the binding energy, the La bond on the surface is recognized as La_2O_3 with small amounts of $La(OH)_3$ [1–5]. Metallic La ($E_b = 836$ eV) remains in the sublayer, where a limited amount of La_2O_3 coexists. The Ni $2p_{1/2}$ core level was used to identify the chemical state. Ni exists in the metallic state in the sublayer ($E_b = 870$ eV) [1]. Al exists in the form of Al_2O_3 ($E_b = 73.7$ eV) judging from the Al 2p peaks. After argon-ion sputtering, metallic Al ($E_b = 72.0$ eV) appears. The surface of the untreated alloy was further analysed by SIMS. The results are shown in Fig. 3 (upper part). La^{3+}, LaO^+ and $La(OH)^{2+}$ were observed. The results are in agreement with the XPS analysis.

La $3d_{5/2}$, Ni $2p_{1/2}$ and Al 2p core levels were determined after F treatment. The results are shown in Fig. 2. The La $3d_{5/2}$ core level was observed to be a single peak at $E_b = 838$ eV which is entirely different from the observations on the untreated surface. The La on the treated surface is not La_2O_3 or $La(OH)_3$ by comparison with the spectra of the untreated surface. It may be LaF_3 (unfortunately, no reference was available for comparison) judging from the quantitative analysis where the atomic ratio of La to F was determined to be 1:3. Further evidence was obtained from SIMS analysis. Figure 3 shows that the surface is covered mostly by LaF_3 judging from the existence of LaF^{2+} and LaF_2^+ species. LaO^+ and $La(OH)^{2+}$ were also observed, but with very low intensity. By extending the sputtering time, the La $3d_{5/2}$ core level spectrum splits into two species. This indicates the appearance of La_2O_3 and metallic La. This is believed to originate from an oxide which was formed during the original sample exposure to air and which remains unreacted even after treatment. The oxide is believed to disappear at longer treatment times. For Ni, the shape and position of the Ni $2p_{1/2}$ spectrum were the same before and after treatment, and it was identified as metallic Ni ($E_b = 870$ eV). Al was found to exist mainly in the form of $Al(OH)_3$ and Al_2O_3 on the surface.

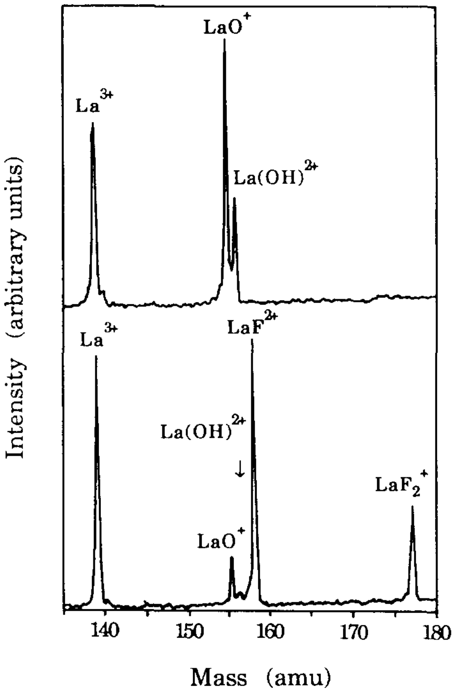


Fig. 3. Secondary ion mass spectra for F-treated and untreated $LaNi_{4.7}Al_{0.3}$ alloy: upper part, untreated surface; lower part, F-treated surface.

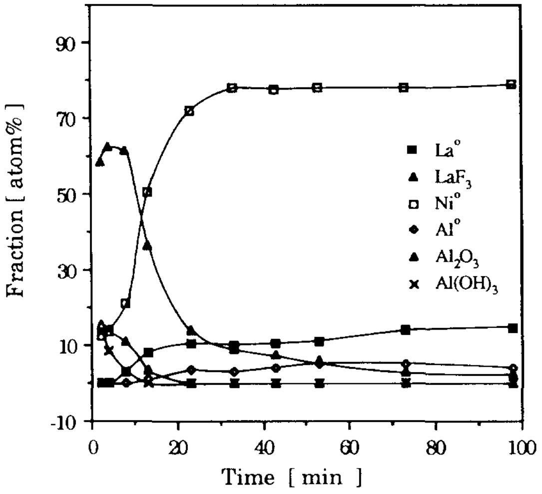


Fig. 4. XPS depth profile of F-treated $LaNi_{4.7}Al_{0.3}$ alloy.

The segregation of elements during treatment was examined by Ar^+ sputtering for various time periods. The depth profiles are shown in Fig. 4. It can be seen that the outer layer is greatly enriched in La and contains little Ni. After 50 min of sputtering, the ratio of La:Ni:Al remains unchanged from the initial bulk composition. This indicates that La segregates to the surface from the $LaNi_{4.7}Al_{0.3}$ phase during treatment. The segregated La combines with F^- to form LaF_3. The Ni precipitates in the sublayer (a limited amount of Ni is dissolved into the F-containing solution). Although the total amount of Ni seems to decrease after F treatment (see Figs. 2 and 4), judging from the atomic ratio of metallic La to metallic Ni as shown in Table 1, the sublayer is an "Ni-rich layer" where free Ni exists. For comparison, the atomic ratio of metallic La to metallic Ni for the untreated surface is shown in Table 2. It can be seen that the amounts of free metallic Ni in the sublayer for the untreated surface are much less than for the F-treated surface.

In summary, the surface structure and composition are changed by the F treatment. The major differences between the treated and untreated surfaces are listed in Table 3.

The surface structure of the F-treated alloy was derived from the above results to have a composition profile as shown schematically in Fig. 5. After the F treatment, an LaF_3 layer is formed on the surface and metallic Ni segregates from the $LaNi_{4.7}Al_{0.3}$ phase and exists in the sublayer. This "free Ni" distributed in the LaF_3 layer may promote an unusually rapid hydrogen uptake during the initial activation procedure by acting as an $H_2 \rightarrow 2H$ dissociation catalyst [5].

TABLE 1. Atomic ratio of metallic La to metallic Ni of the chemically treated $LaNi_{4.7}Al_{0.3}$ surface

Sputtering time (min)	La^0	Ni^0
1	–	Free Ni
2	–	Free Ni
3	1.0	19.4
4	1.0	6.8
8	1.0	7.1
13	1.0	6.3
23	1.0	6.8
33	1.0	7.6
43	1.0	7.3
53	1.0	7.0
73	1.0	5.3
98	1.0	5.0

TABLE 2. Atomic ratio of metallic La to metallic Ni of the untreated $LaNi_{4.7}Al_{0.3}$ surface

Sputtering time (min)	La^0	Ni^0
1	1.0	9.4
2	1.0	9.5
3	1.0	6.5
4	1.0	6.7
13	1.0	6.6
23	1.0	6.8
33	1.0	6.6
48	1.0	6.3

TABLE 3. Differences between the treated and untreated surfaces

Untreated surface	Treated surface
Very smooth surface	Fine net-like structures
Top surface is covered by La_2O_3 with a limited amount of $La(OH)_3$	LaF_3 is formed and almost no La_2O_3 or $La(OH)_3$ on the top surface
Ni element exists as NiO or $Ni(OH)_2$ on the top surface	Litle or no Ni element on the top surface
Only limited amounts of free metallic Ni in the sublayer	Free metallic Ni-rich sublayer

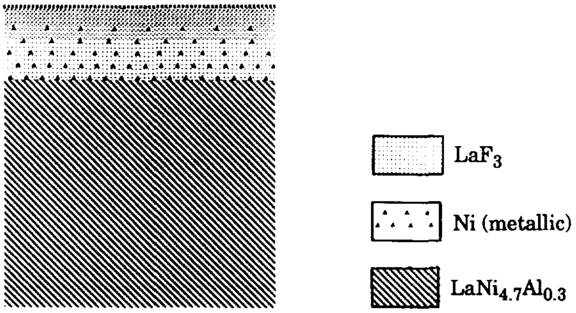


Fig. 5. Schematic model for the surface structure of F-treated $LaNi_{4.7}Al_{0.3}$ alloy.

4. Conclusions

After F treatment, $LaNi_{4.7}Al_{0.3}$ exhibits a fine net-like structure of crystallites of less than 1 μm and segregation of the alloy components takes place on the surface. An LaF_3 layer is formed, and metallic Ni dissociates from the alloy phase and precipitates in the sublayer. The Ni-rich layer works catalytically to decompose H_2 molecules to atoms. This surface property is considered to be related to the excellent reactivity to hydrogen uptake in an initial activation procedure. This method may have potential in the search for new hydride-forming materials and in the promotion of their application [6].

Acknowledgments

The authors are grateful to Dr. G. D. Sandrock for many valuable discussions and to the Japan Research & Development Corporation (JRDC) for funding. They also wish to thank Mr. M. Uchida for the determination of the specific surface area and Mr. H. Watanabe and Mr. A. Inoue for experimental assistance.

References

1 P. Selvam, B. Viswanathan, C. S. Swamy and V. Srinivasan, *Int. J. Hydrogen Energy, 16* (1991) 23.
2 J. H. Waver, A. Franciosi, W. E. Wallace and H. K. Smith, *J. Appl. Phys., 51* (1980) 5847.
3 S. Suda, *Proc. 24th Fall Meeting of the Society of Chemical Engineers, Tokyo, Japan, 1991*, Vol. II, Society of Chemical Engineers, Tokyo, Japan, 1991, p. 383.
4 F. J. Liu, G. Sandrock and S. Suda, *J. Alloys Comp.*, in press.
5 H. C. Siegmann and L. Schlapbach, *Phys. Rev. Lett., 40* (14) (1978) 972.
6 S. Suda and G. Sandrock, *Int. Symp. on Metal–Hydrogen Systems — Fundamentals and Applications, June 8–12, 1992, Uppsala, Sweden, Z. Phys. Chem.*, in press.