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The effect of substitutional elements (Al, Co) in $LaNi_{4.5}M_{0.5}$ on the lattice defect formation in the initial hydrogenation and dehydrogenation

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ABSTRACT

The formation of the vacancy and dislocation by the initial hydrogenation and dehydrogenation in $LaNi_{4.5}M_{0.5}$ (M = Al, Co, and Ni) was observed by means of the positron lifetime technique. The concentrations of vacancy introduced by these processes were 0.25, 0.13 and 0.01 at.% for $LaNi_5$, $LaNi_{4.5}Co_{0.5}$ and $LaNi_{4.5}Al_{0.5}$, respectively. Al substitution into $LaNi_5$ significantly prevented from vacancy formation, compared with $LaNi_5$ and $LaNi_{4.5}Co_{0.5}$. In $LaNi_{4.5}Al_{0.5}$, the increase of the hardness and the enhancement of the pulverization, i.e. enhancement of the formation of micro cracks compared with $LaNi_5$ were observed while the Co substitution had little effect on pulverization and hardness as well as vacancy formation. These results show that the formation of micro cracks became more active process by Al substitution than the formation of the lattice defects to release the strain energy generated by the hydride formation because of the higher formation energy of the lattice defects in $LaNi_{4.5}Al_{0.5}$, although both the formation of micro cracks and lattice defects were still observed in all alloys we studied.

1. Introduction

Hydrogen absorbing alloys are one of the most promising media for onboard hydrogen storage of fuel cell vehicles because of the higher volume density of hydrogen than pressurized gas (35 MPa of hydrogen) and liquid hydrogen. For the practical applications, however, weight density of hydrogen and durability of hydrogen storage capacity must be improved. These hydrogenation properties have been generally improved by the substitution of constitutional elements by other elements [1,2].

Recently, the lattice strain and defect structure introduced by the initial hydrogenation and dehydrogenation in $LaNi_5$ have been investigated by TEM observation and X-ray/neutron diffraction method [3–10] to clarify the hydrogen storage mechanism. They reported the formation of huge amount of dislocation. In addition, using the positron lifetime technique not only the formation of dislocation but also vacancy formation by the initial hydrogenation and dehydrogenation in $LaNi_5$ were observed [11]. Nakamura et al. reported that introduction of the lattice strain influenced by the substitutional elements as well as the hydrogenation properties [12,13]. The substitution of the small amount of Al or Sn showed little peak broadening in XRD profiles even after the hydrogenation, although the significant anisotropic peak broadening was observed in $LaNi_5$ after the hydrogenation [12,13]. These results clearly show that substitution of Al or Sn into $LaNi_5$ influences not only hydrogenation properties but also the introduction and/or accumulation of lattice strain by the hydrogenation and dehydrogenation.

In this paper, the effect of substitutional elements on the lattice defect structure in $LaNi_{5-x}M_x$ (M = Al, Co, and Ni) has been investigated by the positron lifetime technique which can detect both vacancy and dislocation.

2. Experimental procedures

$LaNi_{4.5}M_{0.5}$ (M = Al, Co, and Ni) alloys provided from Chuo Denki Kogyo Co., Ltd. were prepared by high-frequency induction melting. Annealing was performed at 1373 K for 10 h in an Ar atmosphere for homogenization. After crushing of the alloys, annealing was done at 1223 K for 5 h in vacuum to remove the lattice defects introduced by crushing. The initial hydrogenation and dehydrogenation were performed in $LaNi_{4.5}M_{0.5}$ alloys as following conditions. The hydrogenation temperature and pressure were at 296 K and 7 MPa of hydrogen whose purity is 99.99999%. The dehydrogenation was performed under vacuum at 296 K.

In order to evaluate the types and concentration of the lattice defects formed by the initial hydrogenation, isochronal annealing for $LaNi_{4.5}M_{0.5}$ after dehydrogenation was carried out under vacuum. The temperature range of the annealing was from 373 to 1223 K. Each annealing step was 50 K and the annealing time was 900 s. After each annealing, positron lifetimes were measured at 296 K using a positron

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Table 1
Mean positron lifetimes before and after the initial hydrogenation and dehydrogenation in $LaNi_{4.5}M_{0.5}$

	$LaNi_5$	$LaNi_{4.5}Co_{0.5}$	$LaNi_{4.5}Al_{0.5}$
Before	126 ps	121 ps	129 ps
After	198 ps	193 ps	181 ps

lifetime spectrometer with a time resolution of 204 ps. Each positron lifetime spectrum consists of more than 10^6 counts and several spectra were accumulated for each measuring point in order to ensure the reproducibility of the data. The source correction and the resolution functions were evaluated using the code Resolution Program [14]. Lifetime spectra were analyzed using the Positronfit Extended Program [15,16].

Pressure-composition (PC) isotherms were measured at 298 K in the annealed crushed powders of $LaNi_{4.5}M_{0.5}$. The distributions of particle size in $LaNi_{4.5}M_{0.5}$ after the hydrogenation and dehydrogenation process were measured in the solution of glycerin in water using the laser beam (SHIMADZU: SA-CP3L). For the distribution measurement of particle size, the annealed $LaNi_{4.5}M_{0.5}$ with bulk state were hydrogenated and dehydrogenated at 296 K and 7 MPa of hydrogen to reduce the effect of the starting size of $LaNi_{4.5}M_{0.5}$ on the final particle size. The dynamic ultra micro hardness measurements in bulk state of $LaNi_{4.5}M_{0.5}$ before the hydrogenation were performed (SHIMADZU: DUH-W201). The deformation depths of the alloys were measured with increasing of the additional stress up to 2000 mN.

3. Results and discussion

The mean positron lifetimes in fully annealed $LaNi_5$, $LaNi_{4.5}Co_{0.5}$ and $LaNi_{4.5}Al_{0.5}$ were 126, 121 and 129 ps, respectively, as shown in Table 1. These values well consisted with the previous experimental positron lifetime (122 ps) in fully annealed $LaNi_5$ and calculated one (125 ps) in $LaNi_5$ [11,17]. It means that these fully annealed alloys had no lattice defects. It has reported that Co atoms are substituted for both 2c and 3g positions of Ni sites in $LaNi_5$ while Al atoms preferentially are substituted only for the 3g position of Ni site [4,18]. However, the substitution site and elements in $LaNi_5$ had little effect on the positron lifetime.

After the initial hydrogenation and dehydrogenation, the mean positron lifetimes increased by more than 50 ps and were 198, 193 and 181 ps in $LaNi_5$, $LaNi_{4.5}Co_{0.5}$ and $LaNi_{4.5}Al_{0.5}$, respectively. In general, the mean positron lifetime increases mainly by the formation of the lattice defects and/or by the increase of the lattice constant. However, it was reported that the lattice constants did not change so much between before the initial hydrogenation and after dehydrogenation in these alloys [7]. Therefore, these increases of the mean positron lifetimes were originated from the formation of the lattice defect. The mean positron lifetimes after the dehydrogenation were higher than the calculated positron lifetimes of vacancies in the 2c and 3g positions of Ni sites in $LaNi_5$ (166–177 ps) and much lower than the calculated positron lifetime of vacancy in La position in $LaNi_5$ (241 ps) [17]. It suggests that not only mono-vacancy but also larger vacancy cluster such as di- or tri-vacancy formed by the vacancies in Ni sites were introduced by the initial hydrogenation and dehydrogenation.

Fig. 1 shows the mean positron lifetime change during the isochronal annealing in $LaNi_{4.5}M_{0.5}$ after the initial hydrogenation and dehydrogenation. In $LaNi_5$ the mean positron lifetime increased up to 240 ps from 423 to 623 K and then decreased down to 170 ps from 623 to 723 K. This behavior of the mean positron lifetime was explained by the vacancy migration and clustering. Therefore, these results clearly show that vacancies were introduced by the initial hydrogenation and dehydrogenation. This agrees well with our previous report [11]. The mean positron lifetime change against the annealing temperature in $LaNi_{4.5}Co_{0.5}$ was identical to that in $LaNi_5$. It means that $LaNi_{4.5}Co_{0.5}$ had the same defect structure after the dehydrogenation as $LaNi_5$. Co substitution did not influence the lattice defect formation. In $LaNi_{4.5}Al_{0.5}$, the mean positron lifetime also increased and then decreased in the same temperature range. However, magnitude of the mean positron lifetime change was much smaller than that in $LaNi_5$ and $LaNi_{4.5}Co_{0.5}$ during the isochronal annealing. This result indicates that vacancies were also introduced in $LaNi_{4.5}Al_{0.5}$ by the initial hydrogenation and dehydrogenation but $LaNi_{4.5}Al_{0.5}$ had the lower vacancy concentration than $LaNi_5$.

Above 773 K, the mean positron lifetimes in $LaNi_{4.5}M_{0.5}$ studied gradually decreased. However, the mean positron lifetimes even after the annealing at 1273 K were still much higher than that in fully annealed $LaNi_5$. It means that another type of the lattice defects with the higher migration temperature than vacancy was also introduced by the initial hydrogenation and dehydrogenation and some of them were settled down even after the annealing at 1273 K.

To clarify the lattice defect structure in details, the multi-component analysis for the positron lifetime spectra obtained during the isochronal annealing were performed, as shown in Fig. 2. The positron lifetime spectra that were obtained in the temperature range below 723 K in $LaNi_{4.5}M_{0.5}$ studied were decomposed into two components, more than 200 and 160 ps. The former value was much higher than the positron lifetimes for the vacancies of Ni sites (166–177 ps) in $LaNi_5$ and much lower than that for the vacancy of La site (241 ps) in $LaNi_5$ [17]. According to our previous theoretical calculation, the positron lifetime component of 200 ps must come from di-vacancy cluster formed by the vacancies of Ni sites, as shown in Fig. 3 [17]. This increased up to around 400 ps and its relative intensity went down to zero with increase of annealing temperature up to 723 K. The onset temperature for the increase of positron lifetime agrees well with the previous results for vacancy migration temperature in $LaNi_5$ [11]. This behavior was explained by the vacancy migration and clustering. In addition, this result shows that vacancies were aggregated and became larger vacancy clusters during the recovery process of introduced vacancy. Kisi et al. suggested the formation of the finite defects such as small dislocation loops and vacancies from the viewpoints of the anomalous change of *c*/*a* ratio at around 500 K in $LaNi_5$. Our finding clearly shows that this anomalous change of *c*/*a* ratio was originated from the vacancy formation. On the other hand, the latter value (160 ps) was intermediate between fully annealed alloy (122–125 ps) and

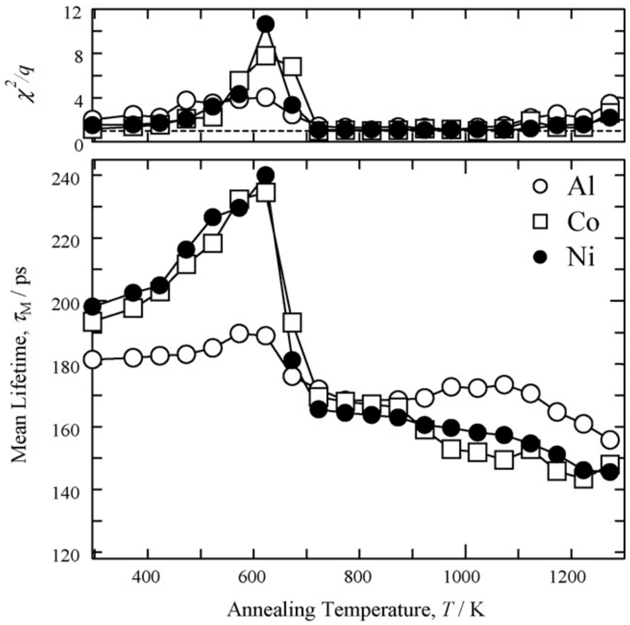

Fig. 1. Positron lifetime during isochronal annealing in $LaNi_{4.5}M_{0.5}$ after the initial hydrogenation and dehydrogenation.