



1.2.2 POSITRON ANNIHILATION STUDY OF HYDROGEN STORAGE ALLOYS

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Abstract

Some AB₃ and AB₂ hydrogen storage alloys have been characterized by using positron-annihilation lifetime spectroscopy. It has been shown that they contain no constitutional vacancies and that deviations from the stoichiometric compositions are all compensated by antistructure atoms. Positron lifetimes in fully-annealed LaNi_{5-x}Al_x and MmNi_{5-x}Al_x alloys show good correlation with their hydrogen desorption pressures. On the other hand, surprising amounts of vacancies together with dislocations have been found to be generated during the first hydrogen absorption process of LaNi₅ and ZrMn₂. These lattice defects play important role in hydrogen absorption-desorption processes of hydrogen storage alloys.

Keywords: positron annihilation, vacancy formation, LaNi₅, ZrMn₂, hydrogen storage alloys

1. Introduction

The positron is a unique probe to study the behaviour of the proton in hydrogen-absorbing matters, for both particles have the same positive elementary charge. In perfect crystals, positrons delocalise in interstitial sites and annihilate with electrons there, since positrons are strongly repelled by ion cores due to the Coulomb repulsion, as are protons. Then, positron annihilation characteristics are determined by the local electronic structure at the interstitial sites, where protons also stay stably.

When there exist vacancies, vacancy clusters or dislocations, which have lower densities of ion cores than the surroundings, positrons are trapped in such defects like protons and annihilate with electrons in the defects. Positron-annihilation characteristics in defects are unique for each kind of defects, and make it possible to identify existing defects with which protons should have strong interactions.

Thus the positron should be a quite unique probe that gives us direct information from the standpoint of the proton about hydrogen storage materials and their structural changes during hydrogen absorption and desorption processes. In this respect we have applied positron lifetime spectroscopy to study some AB₃ and AB₂ hydrogen absorbing alloys.

2. Positron Annihilation

In condensed matter, each positron annihilates with an electron, producing gamma rays, in a very short time. The annihilation rate (λ) is proportional to the electron density at the

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annihilation site. Positron lifetimes τ ($= \lambda^{-1}$) in well-annealed metallic materials are characteristic of each material and in the range of $1-2 \times 10^{-10}$ sec.

In a perfect crystal, a thermalized positron is delocalized (in a Bloch state). The density has maxima in the interstices, since a positron is strongly repelled by ion cores due to the Coulomb repulsion. When there exist vacancies, vacancy clusters or other defects that have lower densities of ion cores than the surroundings, positrons are trapped in the defects and annihilate there. In such defects, positron lifetime is longer, because electron density (both conduction and core electrons) is lower. The positron annihilation characteristics are unique for each kind of defects, and thus make us possible to identify each kind of defects.

For positrons annihilating in a perfect lattice, the decay is simple exponential; the positron lifetime spectrum $T(t)$ has the form

$$T(t) = (I_0/\tau_0)\exp(-t/\tau_0) + (I_d/\tau_d)\exp(-t/\tau_d), \quad (1)$$

where the τ_0 is the positron lifetime in the perfect lattice. When positron-trapping centers such as vacancies exist in the lattice, some positrons are trapped and annihilate in them. According to the so-called trapping model [1-3], the positron lifetime spectrum well approximates to two discrete components:

$$T(t) = (I_0/\tau_0)\exp(-t/\tau_0) + (I_d/\tau_d)\exp(-t/\tau_d). \quad (2)$$

The second term is the defect component. The decay constant τ_d is the positron lifetime in the defect, which is characteristic of each kind of defects. The relative intensity of the defect component, I_d , increases with the defect concentration ($I_0 + I_d = 1$). The first decay constant τ_0 is always shorter than τ_1 [4,5].

Above treatment is readily extended to the cases in which more than two kinds of defects are included [4,5]. Thus, by measuring and analyzing positron lifetime spectra, information on the nature and concentration of defects can be obtained; the defect nature via τ_d and the concentration via I_d . In the case of microvoids, positron lifetime τ_d increases with the number of vacancies that constitute the microvoids, and is asymptotic to 500ps [6]. Positron lifetime at dislocations is not longer than that in monovacancies and changes with the magnitude of the Burger's vector [7].

The positron sensitivity to such defects is quite high: In the case of vacancies, a concentration of 10^{-6} in atomic fraction is enough to be detected; 10^{-4} vacancies make observed positron annihilation characteristics saturated. The sensitivity to vacancy clusters and secondary defects is even higher. This distinctive character is especially noteworthy, since the fraction of a defect's signal is equal to the defect fraction in almost all experimental methods other than positron annihilation. Positrons are able to amplify the signal of defects by a factor of order of 10^4 .

We measured positron lifetime spectra in some hydrogen absorption materials using fast-fast coincidence systems. The instrumental time resolutions were 190-240ps FWHM (full width at half maximum of the resolution function). Measured lifetime spectra were analyzed, after correcting for a small source component, in terms of one, two or three components, using the computer programs Resolution [8] and Positronfit Extended [9]. Other experimental details will be published elsewhere.

3. Defect Structure in Some AB₅ and AB₂ Hydrogen Storage Intermetallics

In intermetallic compounds and ordered alloys, different atomic species occupy differently designated lattice sites and they are usually held together by strong bonds. If an intermetallic compound or an ordered alloy has an extended phase field, its nonstoichiometry may give rise to the existence of constitutional defects such as atoms occupying atomic sites of a sublattice other than its own sublattice (antisite atoms) or vacancies of deficient atomic

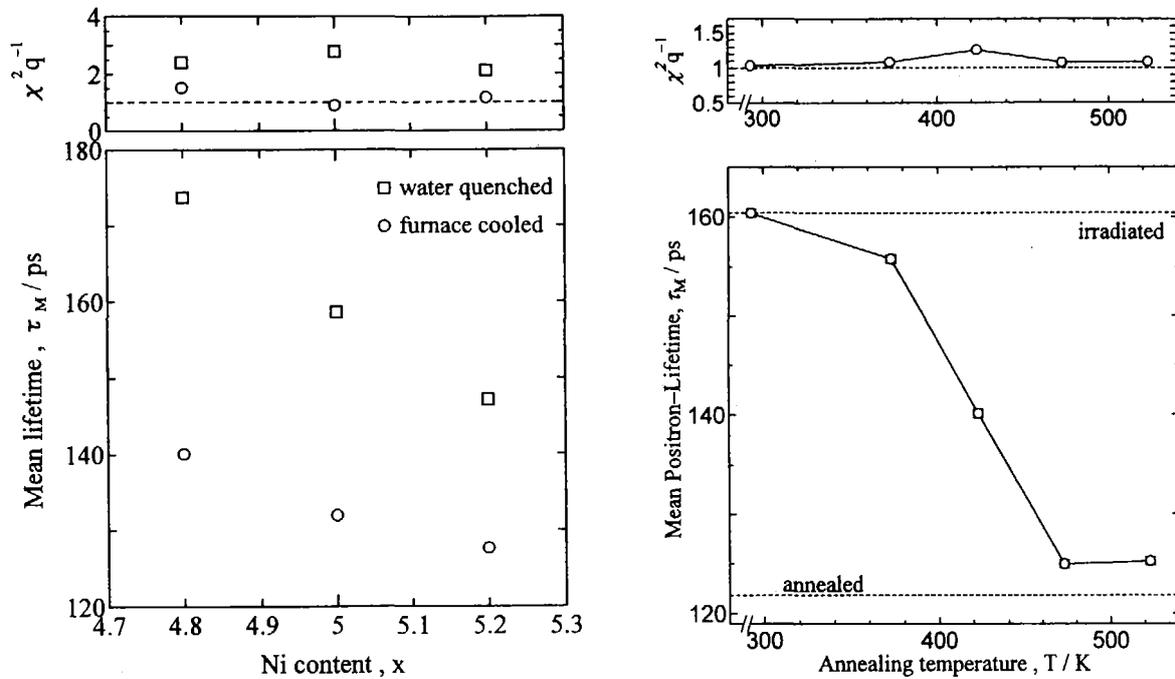


Fig. 1 Positron mean-lifetime in LaNi₅, LaNi_{4.8} and LaNi_{5.2} before and after quenching from 1473K. The variance of the fit $\chi^2 q^{-1}$ is also indicated. (Left)

Fig. 2 Recovery of vacancies in LaNi₅ irradiated with 8MeV electrons at ambient temperature up to 1×10^{17} e/cm². The variance of the fit $\chi^2 q^{-1}$ is also indicated. (Right)

species (constitutional vacancies). It is well known that the type and quantity of constitutional defects directly affect mechanical properties and atomic diffusion in the host ordered materials. Which of these defects dominates the defect structure of the nonstoichiometric compound depends on the crystal structure, constituent elements, and bonding nature of the compound as well as on which of the constituent elements is deficient and the amount by which the compound is non stoichiometric [10].

Which kind of constitutional defects exist in a given compound is easy to distinguish by using the positron lifetime measurement. Positron lifetime values in intermetallic compounds directly reflect their defect structures. For example, Fig.1 shows the positron lifetime resulting from a single-component analysis of experimental spectra obtained for stoichiometric LaNi₅, Ni-poor (LaNi_{4.8}) and Ni-rich (LaNi_{5.2}) samples (prepared by arc-melting of 3N La and Ni). Positron mean lifetime in water-quenched sample is substantially higher than that in furnace cooled sample for all compositions. This is due to the positron trapping by excess vacancies that are quenched from high temperature. In Fig. 1 the variance of the fit $\chi^2 q^{-1}$ is also shown as a measure of the fitting accuracy of the analysis; in case where the quantity of $\chi^2 q^{-1}$ is significantly larger than unity, the measured spectrum is not adequately fitted by the analysis [8,9]. Larger values of the variance for quenched samples also indicate the existence the defect component besides the matrix component.

From this measurement, we can readily conclude that there are no constitutional vacancies in stoichiometric and non-stoichiometric LaNi₅. This is because, if constitutional vacancies exist, all positrons are trapped in such constitutional vacancies even at low temperatures (the concentration of constitutional vacancies is generally much higher than that of thermal vacancies) and no such changes as shown in Fig. 1 should be observed. In the same manner, defect structures can be readily judged by thermal equilibrium positron lifetime measurement at high temperatures or by comparing positron lifetime before and after electron-irradiation

[11].

A LaNi_5 sample (purity; 99.9wt%, made by High-Purity Chemicals Co.Ltd.) was irradiated with electrons of 8MeV up to $1 \times 10^{17} \text{e}/\text{cm}^2$ at ambient temperature. Positron mean lifetime was increased from 122ps to 160ps by the irradiation, which shows clearly that the LaNi_5 does not contain any constitutional vacancies. Fig. 2 shows the recovery of radiation-induced vacancies in LaNi_5 during the subsequent isochronal annealing (900s/50K) in Ar. This observation makes it clear that vacancies in LaNi_5 become mobile around 423K and migrate to permanent sinks such as dislocations, grain boundaries and free surfaces.

Similar results have been obtained for $\text{LaNi}_{5-x}\text{Al}_x$ ($x = 0, 0.1, 0.5$), $\text{MmNi}_{5-x}\text{Al}_x$ ($x = 0, 0.1, 0.5$), $\text{La}_{1-x}\text{Ca}_x\text{Ni}_5$, $\text{Mm}_{1-x}\text{Ca}_x\text{Ni}_5$, ZrMn_2 , $\text{ZrMn}_{2-x}\text{Co}_x$, $\text{ZrMn}_{2-x}\text{Ni}_x$. All these intermetallic compounds have no constitutional vacancies. In other words, their nonstoichiometries are always compensated with anti-site atoms. Until now, B2 compounds, such as NiAl, NiGa, CoAl, CoGa, CoTi, seem to be unique examples in which the existence of vacancies compensating nonstoichiometry has been proved by using positron annihilation lifetime method [9].

4. Lattice Defects Induced by Hydrogen Absorption

Fig. 3 shows positron lifetime changes during the first hydrogen absorption process of LaNi_5 (purity; 99.9%, made by High-Purity Chemicals Co. Ltd.) at ambient temperature. The abscissa indicates the hydrogen content H/M . The positron lifetime increases steeply and shows a saturation behavior. This increase cannot be due to the formation of the hydride itself, but should be due to the accompanying irreversible structural change, the introduction of high density of lattice defects, since subsequent hydrogen desorption did not make the positron lifetime recover but caused a further increase.

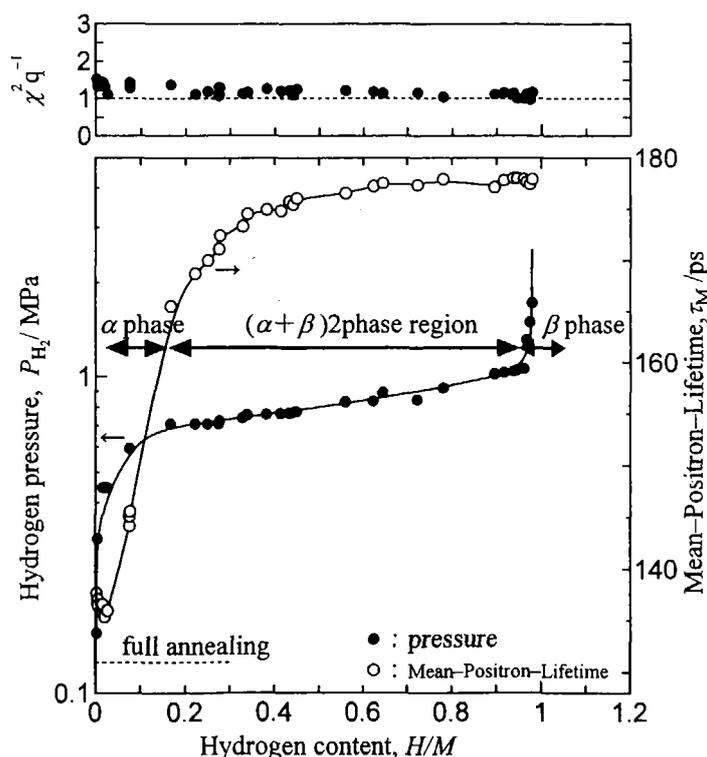


Fig. 3 Positron mean-lifetime change in LaNi_5 during the first hydrogen absorption at ambient temperature. The variance of the fit $\chi^2 q^{-1}$ is also indicated.

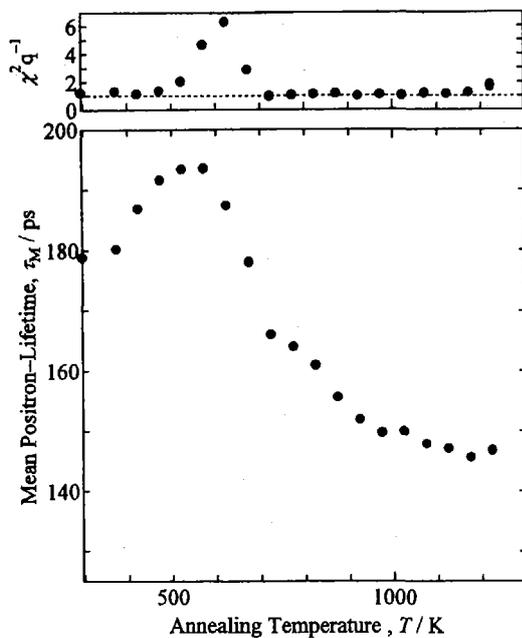


Fig. 4 Positron mean-lifetime change in LaNi_5 during isochronal annealing (15min / 50K) after the first hydrogen absorption-desorption cycle. The variance of the fit $\chi^2 q^{-1}$ is also indicated. (Left)

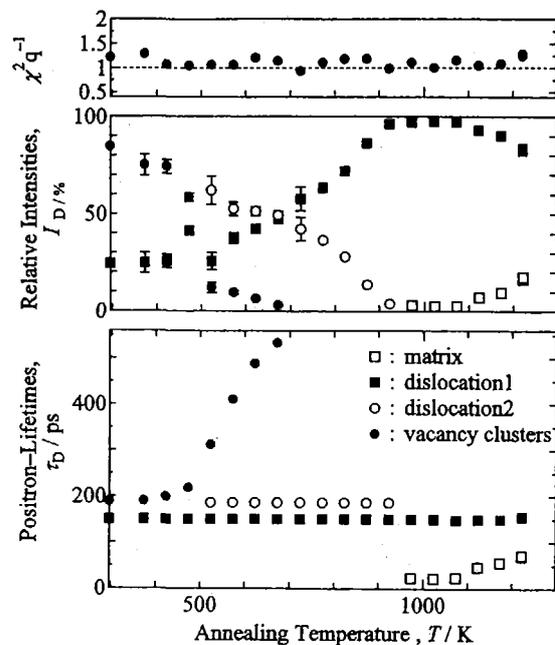


Fig. 5 Result of the component analysis of the lifetime spectra recorded during isochronal annealing of LaNi_5 that has undergone one absorption-desorption cycle. Positron lifetime in each component (lower part) and their relative intensities (upper part). (Right)

The annealing process of the hydrogen-induced defect was studied by positron lifetime measurements in the same specimen during isochronal annealing. The result is presented in Fig. 4. Three recovery stages can be recognized in Fig. 4, around 423K, 823K and 1123K. The most important change is the mean lifetime increase observed above 423K, because this kind of lifetime change is the typical manifestation of void formation by vacancy clustering. The increase in the variance of the fit $\chi^2 q^{-1}$ also indicate the appearance of a new defect-component whose positron lifetime is much higher than co-existing defects. This vacancy-migration temperature in LaNi_5 coincides well with that obtained after electron irradiation (see Fig. 2). This experiment revealed an important fact, that high numbers of excess vacancies are introduced in LaNi_5 by hydrogen absorption. The two other recovery stages in Fig. 4, around 823K and 1123K, are safely attributed to the recovery of two kinds of dislocations by the following multi-component analyses of positron lifetime spectra.

The positron lifetime spectra were decomposed into multicomponents. The results are shown in Fig. 5. The lower part shows positron lifetimes for vacancy clusters, dislocations and the matrix, and the upper part shows the relative intensities of the each component. In this analysis, two dislocation components are resolved.

Just after hydrogen desorption, small vacancy clusters (single vacancies and di- and tri-vacancies at most) and dislocations are observed. Above 423K the positron lifetime of the vacancy-cluster component drastically increase from 200ps to around 500ps. This is the direct evidence for the void formation by the clustering of vacancies that are generated during hydrogen absorption. On the other hand, the relative intensity of the vacancy-cluster component decreases at the same time. This behavior is quite normal since most vacancies and vacancy clusters annihilate at such permanent sinks as dislocations, grain boundaries and surfaces, whose densities are very high after a hydrogen absorption and desorption cycle.

Above 700K, relative intensity of the dislocation component becomes 100%. All positrons are trapped and annihilate at dislocations. This result clearly shows that dislocation density is

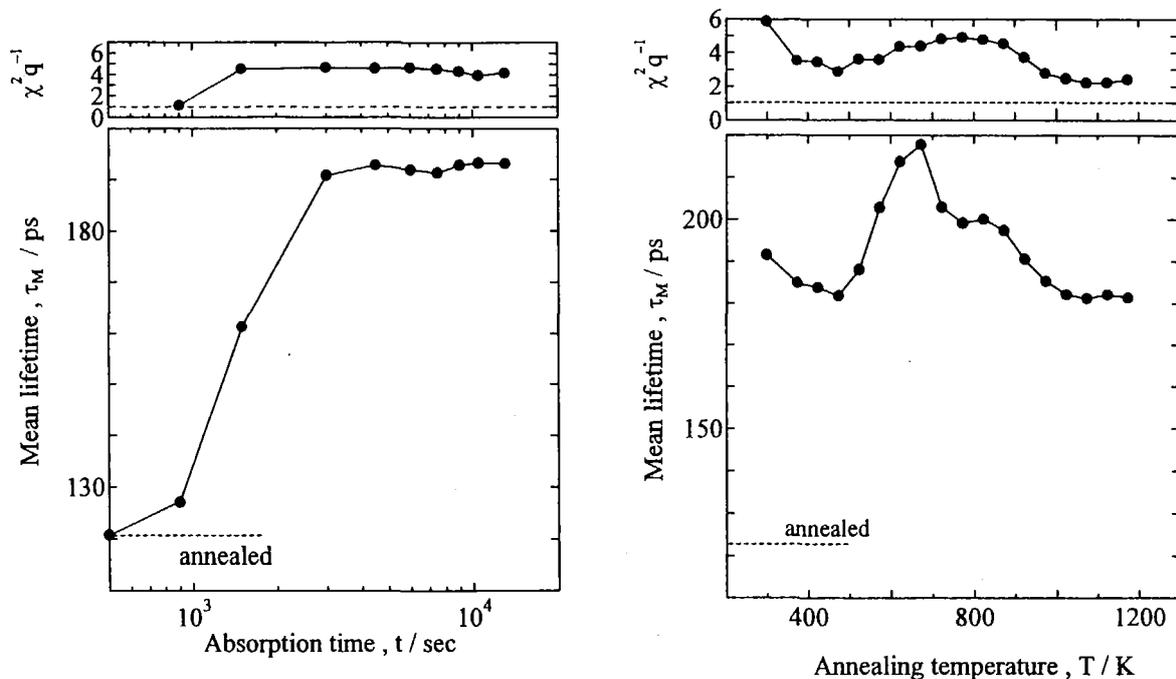


Fig. 6 Positron mean-lifetime change in $ZrMn_2$ during the first hydrogen absorption under a constant hydrogen pressure of 0.5MPa at ambient temperature. The variance of the fit $\chi^2 q^{-1}$ is also indicated. (Left)

Fig. 7 Positron mean-lifetime change in $ZrMn_2$ during isochronal annealing (15min / 50K) after the first hydrogen absorption-desorption cycle. The variance of the fit $\chi^2 q^{-1}$ is also indicated. (Right)

high enough to cause the saturation trapping of positrons even after the disappearance of vacancies and vacancy clusters. The matrix component appears above 1073K at long last. This implies that the vacancy concentration generated by hydrogen absorption is high enough to surpass even a high density of dislocations in trapping positrons. Rough estimation indicates that the vacancy concentration should amount to the order of 10^{-2} .

While there can be no doubt about the vacancy formation in $LaNi_5$ by hydrogen absorption, this leads us to the question of whether the vacancy formation by hydrogen absorption is a specific behavior of $LaNi_5$ or a more general phenomenon. In order to clarify this point we have carried out positron lifetime measurements on $ZrMn_2$ (prepared by arc-melting 99.6wt%Zr and 99.9wt%Mn). Positron lifetime change in $ZrMn_2$ during the first absorption process of hydrogen at ambient temperature under a constant hydrogen pressure of 0.5Mpa is shown in Fig. 6. Fig. 7 demonstrates the positron lifetime change during the subsequent isochronal annealing of the same specimen. All important features are quite similar to those observed in $LaNi_5$: huge numbers of defects, not only dislocations but also vacancies, are formed during hydrogen absorption. Induced vacancies agglomerate during subsequent annealing (around 500K in this compound).

It follows from the observations above that the vacancy formation during hydrogen absorption in hydrogen storage materials should be a rather general phenomenon. More detailed studies including the study of the vacancy formation mechanism are now in progress.

5. Concluding Remarks

The unique characteristics of positron annihilation have been applied to study some AB_5 and AB_2 hydrogen absorbing alloys and the following points have been revealed:

1. In $LaNi_{5\pm x}$ there are no constitutional vacancies due to deviations from the stoichiometric

- compositions. The deviations are compensated by antistructure atoms in these alloys.
2. Huge numbers of excess vacancies are formed in addition to dislocations during the first hydrogen absorption process of LaNi₅ and ZrMn₂.
 3. Excess vacancies introduced in the alloys by hydriding are contained in the specimen at ambient temperature, where vacancies are practically immobile.
 4. Above certain temperatures, excess vacancies become mobile and form microvoids.

Hereafter, defects and their properties in many important and potential hydrogen storage materials will be clarified by using positron annihilation methods and such information will be quite useful to develop hydrogen storage materials and processing.

Acknowledgements

This work is supported partially by a Grant-in Aid for Special-Area Research from the Ministry of Education, Science and Culture, Japan.

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