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Positron annihilation study of lattice defects induced by hydrogen absorption in some hydrogen storage materials

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Abstract

Some AB_5 and AB_2 hydrogen storage compounds 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 $LaNi_5$ and $ZrMn_2$. These lattice defects may play a key role in initial activation processes of hydrogen storage materials.

Keywords: Positron annihilation; Vacancy formation; $LaNi_5$; $ZrMn_2$; Hydrogen storage materials

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 observed 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 AB_5 and AB_2 hydrogen absorbing alloys. Before we present our results, the positron annihilation method, which has been successfully applied to studies of atomic-scale defects in solids, is introduced briefly. The readers are referred to some textbooks [1–3], and to recent proceedings [4–6] for detailed information on the whole area of positron solid-state physics.

2. Positron annihilation

The positron is the antiparticle to the electron. The positron has the same rest mass (m_0) as the electron but the opposite charge; that is, one positive elementary charge. In condensed matter, each positron annihilates with an electron, producing gamma rays, in a very short time (10^{-10}–10^{-9} s). By measuring the angular correlation or the Doppler broadening of the emitted gamma rays, or by measuring the positron lifetime, we can deduce information about the electron momentum distribution or electron density at the positron annihilation sites, which are interstitial sites in crystals or crystal lattice defects of the materials.

In conventional positron annihilation experiments, positrons, which can be readily obtained from such radioactive isotopes as ^{22}Na, ^{58}Co, ^{64}Co, ^{68}Ge, are directly injected into a specimen. The implantation depth of positrons is in the range of 0.1–1 mm, depending on the positron energy and the density of the sample. Hence, positrons deduce in-

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formation of the bulk of a specimen in conventional source experiments. Surface or near-surface information is obtained by use of recently developed slow-positron beam techniques [7–9].

Positrons injected in materials lose their kinetic energy (10^5–10^6 eV depending on source nuclei) and slow down to thermal energies (kT) (thermalization) within a few picoseconds and diffuse in the specimen. Typical diffusion lengths of thermalized positrons are of the order of 10^{-7} m. In condensed matter, nearly all (about 99.7%) positrons annihilate each with an electron into two gammas. Since the total energy and the total momentum are conserved before and after the annihilation of a positron-electron pair, each gamma has energy m_0c^2=0.511 MeV (c is the velocity of light) and is emitted from the annihilation site in one of two almost opposite directions.

The most popular positron source is ^{22}Na, since the half-life of the radioisotope is as long as 2.6 year, and the efficiency of the β^+ decay (positron emission) is as high as 90%. Besides, ^{22}Na is convenient for positron lifetime measurements, because it emits a high-energy γ-ray (1.28 MeV) immediately after the emission of a positron (within a few picoseconds). This γ-ray of 1.28 MeV is practically used as the signal of a positron birth. Positron lifetime is obtained by measuring the time difference between the detection of the 1.28 MeV γ-ray and the detection of 0.511 MeV γ-ray, which is emitted by the positron-electron pair annihilation. The annihilation rate (λ) is proportional to the electron density at the annihilation site. Positron lifetimes τ ($=\lambda^{-1}$) in well-annealed metallic materials are characteristic of each material and in the range of 1–2×10^{-10} s.

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. On the other hand, the angular correlation curve and the Doppler broadening spectrum become narrower and the peak counting rate becomes higher. These 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

$$T(t) = (1/\tau_1)\exp(-t/\tau_1) \qquad (1)$$

where the τ_1 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 [10–12], the positron lifetime spectrum well approximates to two discrete components:

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

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 [13,14].

The above treatment is readily extended to the cases in which more than two kinds of defects are included [13,14]. 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 500 ps [15]. Positron lifetime at dislocations is not longer than that in monovacancies and changes with the magnitude of the Burger's vector [16].

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 190–240 ps 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 either one or two components, using the computer programs Resolution [17] and Positronfit Extended [18]. Other experimental details will be published elsewhere.

3. Defect structure in some AB$_5$ and AB$_2$ 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 non-stoichiometry 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 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 non-stoichiometric 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 [19].

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 $LaNi_5$, Ni-poor ($LaNi_{4.8}$) and Ni-rich ($LaNi_{5.2}$) samples (prepared by arc-melting of 3 N 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 [17,18]. Larger values of the variance for quenched samples also indicate the existence of 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 $LaNi_5$. 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 [20].

A $LaNi_5$ sample (purity; 99.9 wt.%, made by Kojundo Chemical Laboratory Co. Ltd.) was irradiated with electrons of 8 MeV up to 1×10^{17}e cm^{-2} at ambient temperature. Positron mean lifetime was increased from 122 to 160 ps 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 (900 s/50 K) in Ar. This observation makes it clear that vacancies in $LaNi_5$ become mobile around 423 K and migrate to permanent sinks such as dislocations, grain boundaries and free surfaces.

Similar results have been obtained for $LaNi_{5-x}Al_x$ ($x=$ 0, 0.1, 0.5), $MmNi_{5-x}Al_x$ ($x=0$, 0.1, 0.5), $La_{1-x}Ca_xNi_5$, $Mm_{1-x}Ca_xNi_5$, $ZrMn_2$, $ZrMn_{2-x}Co_x$, $ZrMn_{2-x}Ni_x$. All these intermetallic compounds have no constitutional vacancies. In other words, their non-stoichiometries 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 non-stoichiometry has been proved by using positron annihilation lifetime method [18].

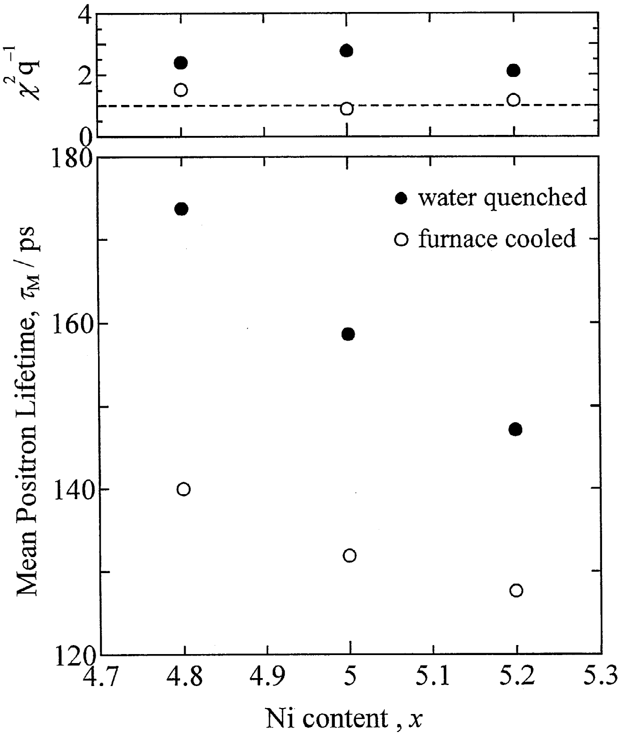

Fig. 1. Positron mean-lifetime in $LaNi_5$, $LaNi_{4.8}$ and $LaNi_{5.2}$ before and after quenching from 1473 K. The variance of the fit $\chi^2 q^{-1}$ is also indicated.

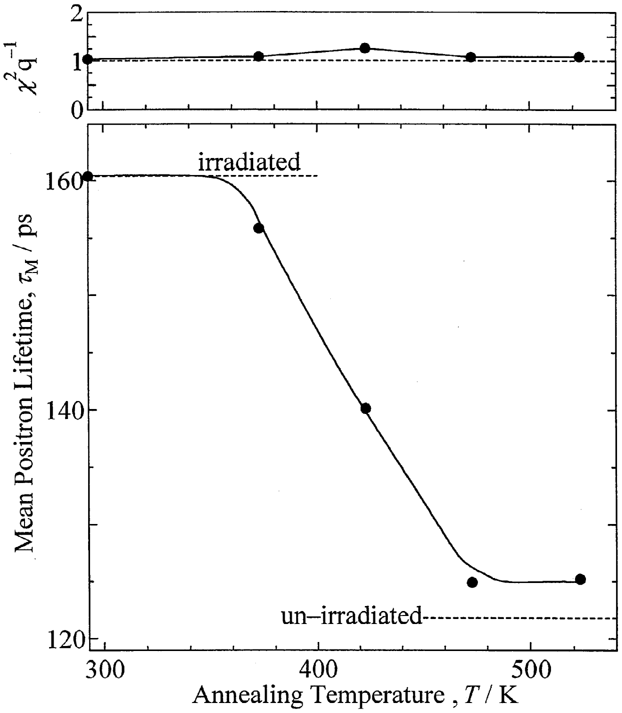

Fig. 2. Recovery of vacancies in $LaNi_5$ irradiated with 8 MeV electrons at ambient temperature up to 1×10^{17} e cm^{-2}. The variance of the fit $\chi^2 q^{-1}$ is also indicated.

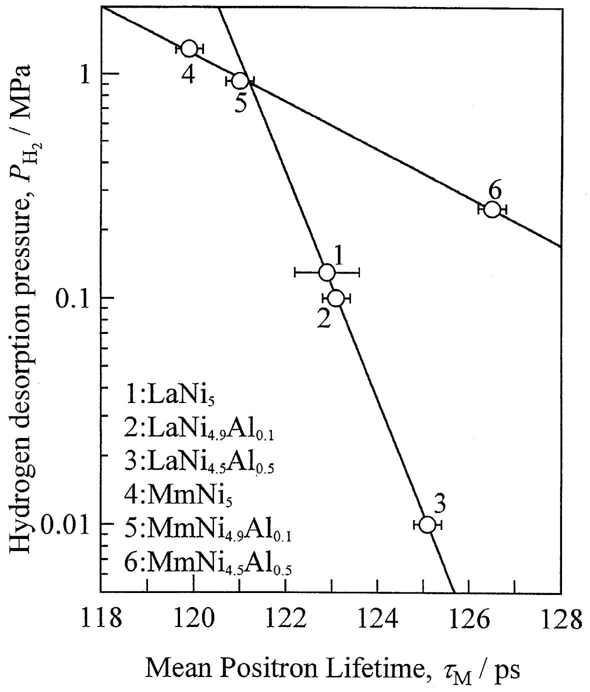

Fig. 3. Hydrogen desorption pressure vs. positron lifetime in $LaNi_{5-x}Al_x$ ($x=0$, 0.1, 0.5) and $MmNi_{5-x}Al_x$ ($x=0$, 0.1, 0.5).

4. Positron annihilation characterization of hydrogen storage properties

Positron lifetimes ware measured in well annealed $LaNi_{5-x}Al_x$ ($x=0$, 0.1, 0.5) and $MmNi_{5-x}Al_x$ ($x=0$, 0.1, 0.5), which were prepared by arc-melting. A good correlation between the positron lifetime and the hydrogen desorption pressure of the alloys has been found as shown in Fig. 3. Positron annihilation characteristics may be used as good indices of some properties of hydrogen absorption materials, since positron annihilation characteristics are determined by the electronic structure at interstitial sites where hydrogen atoms stay.

5. Lattice defects induced by hydrogen absorption

Fig. 4 shows positron lifetime changes during the first hydrogen absorption process of $LaNi_5$ (purity; 99.9%, made by Kojundo Chemical Laboratory Co. Ltd.) at ambient temperature. The abscissa indicates the hydrogen absorption time under a constant hydrogen pressure of 0.6 MPa. After an incubation period 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.

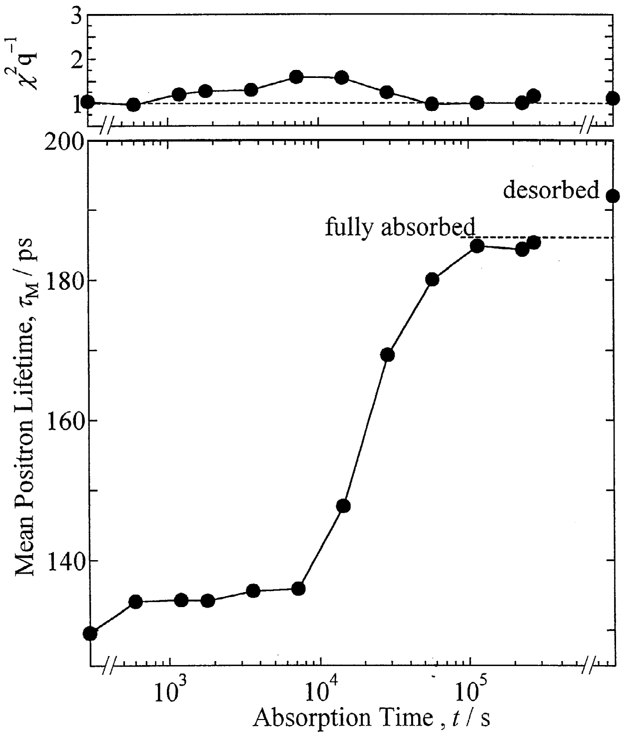

Fig. 4. Positron mean-lifetime change in $LaNi_5$ during the first hydrogen absorption under a constant hydrogen pressure of 0.6 MPa at ambient temperature. The variance of the fit $\chi^2 q^{-1}$ is also indicated.

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. 5. Three recovery stages can be recognized in Fig. 5, around 423, 823 and 1123 K. The most important change is the mean lifetime increase observed above 423 K, 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. 5, around 823 and 1123 K, 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. 6. The lower part shows positron lifetimes for vacancy clusters (~225 ps), dislocations (~175 ps) and the matrix (<130 ps), and the upper part shows the relative intensities of each component. In this analysis, only one dislocation component is resolved since positron lifetime difference in the two kinds of dislocations is rather small.

Just after hydrogen desorption, small vacancy clusters

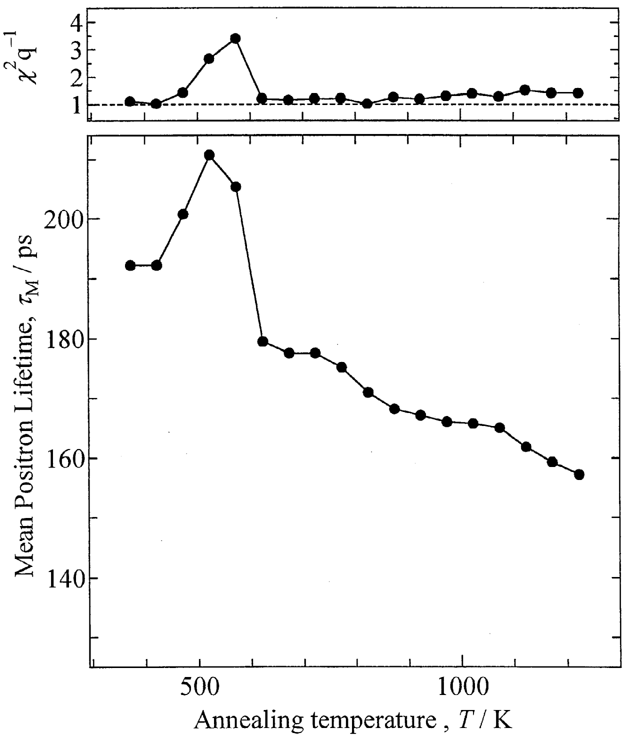

Fig. 5. Positron mean-lifetime change in $LaNi_5$ during isochronal annealing (15 min/50 K) after the first hydrogen absorption–desorption cycle. The variance of the fit $\chi^2 q^{-1}$ is also indicated.

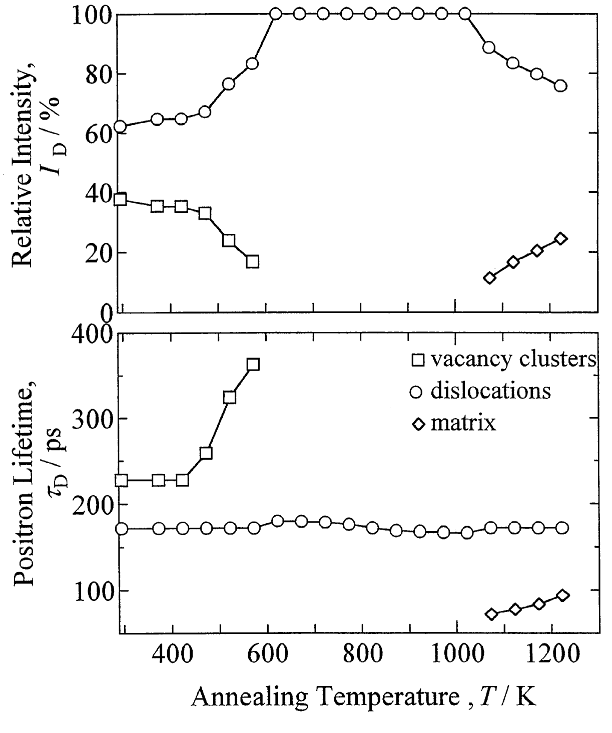

Fig. 6. Result of the component analysis of the lifetime spectra recorded during isochronal annealing of $LaNi_5$ that has undergone one absorption–desorption cycle. Positron lifetime in each component (lower part) and their relative intensities (upper part).

(single vacancies and di- and tri-vacancies at most) and dislocations are observed. Above 423 K the positron lifetime of the vacancy-cluster component drastically increases from 225 to 375 ps. This is direct evidence for 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 623 K, relative intensity of the dislocation component becomes 100%. All positrons are trapped and annihilate at dislocations. This result clearly shows that dislocation density is high enough to cause the saturation trapping of positrons even after the disappearance of vacancies and vacancy clusters. The matrix component appears above 1073 K 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 99.6 wt.% Zr and 99.9 wt.% Mn). Positron lifetime change in $ZrMn_2$ during the first absorption process of hydrogen at ambient temperature under a constant hydrogen pressure of 0.5 MPa is shown in Fig. 7. Fig. 8 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 500 K 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.

6. 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

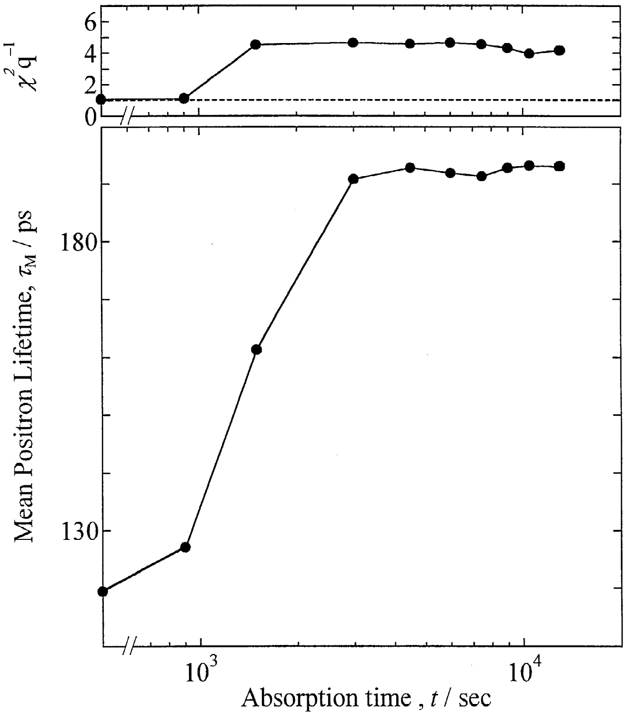

Fig. 7. Positron mean-lifetime change in $ZrMn_2$ during the first hydrogen absorption under a constant hydrogen pressure of 0.5 MPa at ambient temperature. The variance of the fit $\chi^2 q^{-1}$ is also indicated.

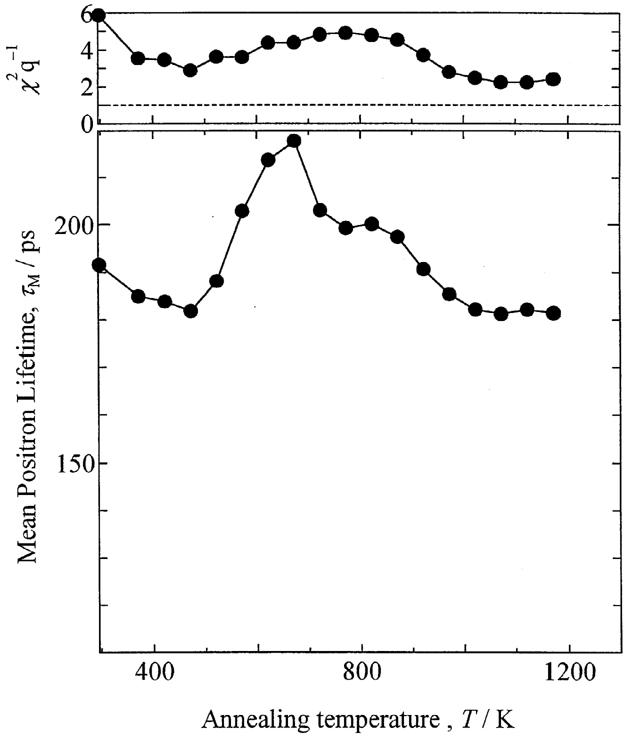

Fig. 8. Positron mean-lifetime change in $ZrMn_2$ during isochronal annealing (15 min/50 K) after the first hydrogen absorption–desorption cycle. The variance of the fit $\chi^2 q^{-1}$ is also indicated.

deviations are compensated by antistructure atoms in these alloys.

2. Positron lifetimes observed in well annealed alloys change systematically with their hydrogen-desorption pressures. Positron lifetime may be useful as a good index of equilibrium hydrogen pressure.
3. Huge numbers of excess vacancies are formed in addition to dislocations during the first hydrogen absorption process of $LaNi_5$ and $ZrMn_2$.
4. Excess vacancies introduced in the alloys by hydriding are contained in the specimen at ambient temperature, where vacancies are practically immobile.
5. 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

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