Importance of starting time for defect analysis using positron annihilation lifetime measurements

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Conventional positron annihilation lifetime measurements have focused on determining the lifetime and relative intensity of each lifetime component deduced by multi-component analysis or the “mean” lifetime deduced by single-component analysis. So far, little attention has been paid towards the starting time (T₀) on the spectrum’s time axis. When analysing lifetime spectra with multiple components using an exponential function with a single-component, there is a difference between the experimental data and the fitted spectrum. Compensating for this difference causes a shift in the T₀ value in the fitted spectrum. This study examines the shifts in T₀ (ΔT₀) in positron lifetime spectrum analyses of metal samples with defects. We conducted simulations of trapping models and experiments with shot-peened stainless steel, verifying that ΔT₀ changed depending on the defect concentration even when almost all positrons were trapped (full trap). Therefore, we propose ΔT₀ as a new parameter for evaluating positron annihilation lifetime measurements. © 2019 The Japan Society of Applied Physics

1. Background of research

Positron annihilation lifetime measurement¹–⁴ is a highly sensitive method used for probing open volume defects in metals and free volumes in polymers. It is used to analyse atomic vacancies and nanometer scale holes in various structural and functional materials.

When positrons are incident on a metal sample without defects, they are all annihilated in the bulk and the positron lifetime spectrum only has a single-component. If the defect, i.e. a single vacancy, is introduced into the metal, some of the positrons will be captured by the defect and have a longer lifetime, causing the positron lifetime spectrum to have two components. In such cases, the lifetime and relative intensity of each component can be obtained by analysing the lifetime spectrum using an exponential function with two components. Applying a trapping model⁵ to the analysis results enables the lifetime, which is correlated with the defect size, and trapping rate, which is proportional to the defect concentration, to be obtained. However, multi-component analyses of positron lifetime spectra are often difficult. For example, various kinds of defects in the sample, such as dislocations, vacancies or voids, can produce several positron lifetime components of only slightly different lifetimes or high defect concentrations can lead to the shortest lifetime component with an unresolvably short lifetime, as in the case of shot-peened stainless steel to be reported in this paper.

When multi-component analyses are difficult, the spectrum is sometimes analysed in terms of an exponential function with a single-component. However, such single-component analyses limit the information that can be obtained. Assuming that the positron lifetime is continuously distributed, i.e. following a log-normal distribution, they can identify the distribution’s width and “mean” lifetime, but this information is hardly sufficient.

Conventional positron annihilation lifetime measurements have focused on the lifetime and intensity of each component deduced by multi-component analysis or “mean” lifetime deduced by single-component analysis, and little attention has been paid towards the starting time (T₀) on the spectrum’s time axis. However, as shown in Fig. 1, when analysing a positron lifetime spectrum with multiple components using an exponential function with a single-component, there is a difference between the spectrum and fitted data. To compensate this difference, T₀ is predicted to shift in the analysis result. In the presence of one-type defects, The T₀ shift is expected to increase from 0 ps, assume a maximum at a certain defect concentration and then return to 0 ps with increasing defect concentration. Yet to accurately measure the change in T₀ (ΔT₀), care must be taken to prevent the time axis shifting from measurement to measurement.

Herein, we used two-state, i.e. bulk and dislocations, and three-state, i.e. bulk, dislocations and vacancies, trapping models to simulate the positron lifetime spectrum. Then, we analysed the positron lifetime spectra obtained using an exponential function with a single-component to obtain the “mean” lifetime and ΔT₀. We also measured the positron annihilation lifetimes of SUS304 stainless steel samples with defects introduced by shot-peening using a system that produces little shift in the time axis (T₀) of the positron lifetime spectrum,⁶ comparing these with simulated results obtained under the same conditions.

2. Simulation evaluation

Using Excel VBA, we created positron lifetime spectra that duplicates the trapping model via Monte Carlo simulations, and analysed the same. Figure 2 shows a block diagram for the simulations, which model the trapping of positrons by one type of defect and their annihilation by two states, i.e. in the bulk and by dislocations. In a similar manner, we also simulated positron annihilation by three states, i.e. in the bulk and by two types of defect (dislocations and vacancies). Figure 3 shows an example of a simulated positron lifetime spectrum.
We used the trapping model to create two-state positron lifetime spectra with bulk and dislocation components and three-state positron lifetime spectra with bulk, dislocation and vacancy components, with trapping rates (given by the product of the specific trapping rate and the defect concentration) ranging from $10^6$ to $10^{13}$ s$^{-1}$. Each lifetime was based on the approximate value for pure steel: 100 ps for positrons annihilated in the bulk, 150 ps for dislocations and 200 ps for vacancies. In addition, the full width at half maximum (FWHM) time resolution was 150 ps, total positron count was 200,000, channel width was 10 ps/ch, and background was 2 counts/ch. In the three-state model, the trapping rates for dislocations and vacancies were the same.

3. Experimental method

Shot-peening$^8$ involves blasting to harden the material’s surface ($<200 \mu m$) by introducing many dislocations. Herein, we used the shot-peening machine shown in Fig. 4 and SUS304 stainless steel samples that had undergone “Bright Annealing” to remove defects. We fixed each sample onto a sample stage on top of a rotating stage to ensure accurate shot-peening. Table I lists the conditions used. We prepared nine different samples by shot-peening for different times, i.e. 0, 12, 36, 72, 120, 240, 480, 960 and 1920 s.

We used a PSA-TypeL-II$^9$ system (Toyo Seiko Co. Ltd.) for the positron annihilation lifetime measurements. This system uses the anti-coincidence (AC) method$^{10-12}$ and, as shown in Fig. 5, it can measure the positron annihilation lifetime of a single specimen. The sample is placed on a stage with a $^{22}$Na positron source ($\sim$0.8 MBq) enclosed in 7.5 $\mu m$.
and the detection signals are used for AC processing. In this way, we can obtain lifetime data only for positrons that are annihilated in the sample and in the source. In this system, the locations of the source, sample stage, two $\gamma$-ray detectors and positron detector are all fixed. Consequently, the time axis rarely shifts from measurement to measurement. In fact, the standard deviation of $T_0$ over five measurements of the SUS304 sample without shot-peening (repeatedly placing the sample and recording 1 M counts) was 0.28 ps.

The measured positron lifetime spectrum was analysed using a single-component, and the “mean” positron lifetime and $\Delta T_0$ were obtained. As for the resolution, the single-Gaussian component was set to be free, whereas the source component lifetime (Kapton’ lifetime) and intensity were fixed as 380 ps and 22%, respectively. The somewhat high intensity of this source component is due to that positrons annihilated in the source are not eliminated by AC processing. The IPALM$^{11}$ software included with the PSA system was used for the analysis.

### 4. Simulated and experimental results

Figure 6 shows a single-component analysis of the simulated positron lifetime spectra, based on assuming that the time resolution is single-Gaussian and treating its half-width as free. Here, the right-hand axis shows “$-\Delta T_0$” since the shifts $\Delta T_0$ from the starting time set by the simulation were negative. The “mean” positron lifetime increased with the trapping rate before reaching a plateau. In the two-state (bulk and dislocations) model, the lifetime increased from 100.2 to 150.9 ps before becoming almost constant. In the three-state (bulk, dislocations and vacancies) model, the lifetime increased from 99.5 to 175.2 ps before becoming almost constant. Meanwhile, the $-\Delta T_0$ values initially increased and then decreased. In the two-state model, they increased from 0.4 to 12.5 ps before decreasing. In the three-state model, they increased from 0.4 to 19.3 ps before decreasing. The $-\Delta T_0$

Table I. Shot-peening conditions.

| Machine type          | Air (gravity) method |
|-----------------------|---------------------|
| Shot particle material | RSCW304 0.3         |
| Shot-peening pressure | 0.2 MPa (gravity method) |
| Shot-peening flow rate| 3.3 kg min$^{-1}$    |
| Sample stage rotation rate | 20 rpm             |
| Distance from injection nozzle to sample | 160 mm         |
| Injection nozzle      | φ9 mm, ceramic      |
| Shot angle to sample  | 90°                 |
| Distance from injection nozzle to sample | 160 mm         |
| Rotating stage speed  | 20 rpm              |
| Rotation angle        | 90°                 |

Fig. 4. (Color online) Shot-peening machine. Shot particles are ejected from the injection nozzle and strike the sample surface. The sample is fixed to a sample stage on the rotation stage. The stage rotates at 20 rpm.

Fig. 5. (Color online) Principle of the anti-coincidence (AC) positron lifetime measurement system, PSA-TypeL-II$^{10}$ system (Toyo Seiko Co. Ltd.). A single sample specimen is mounted on the sample stage, in the centre of which a $^{22}$Na positron source is firmly fixed. The positron lifetimes are measured by determining the time interval between the initial 1.27 MeV $\gamma$-ray, emitted simultaneously with the generation of the positron and the 0.511 MeV annihilation $\gamma$-ray. Positrons emitted directly away from the source and in the source are detected by a plastic scintillator coupled to a photomultiplier tube, the signals from which are used to eliminate the associated annihilation events by anti-coincidence (AC) processing.

Fig. 6. (Color online) “Mean” positron lifetimes and $\Delta T_0$ values obtained by single-component analysis of the simulated positron lifetime spectra. The FWHM of the single-Gaussian resolution function was treated as a fitting parameter. Here, the □ are the “mean” positron lifetimes and the ○ are the $\Delta T_0$ values for the two-state model (bulk and dislocations) simulations. Likewise, the ■ are the “mean” positron lifetimes and the ● are the $\Delta T_0$ values for the three-state model (bulk, dislocations and vacancies) simulations. The source component was not included in these simulations.
values at a trapping rate of $10^{13}$ s$^{-1}$ were 0.2 ps (almost 0 ps) in the two-state model and 2.1 ps in the three-state model. The incomplete recovery of $\Delta T_0$ in the three-state model is likely due to the multi-component nature of the positron lifetime spectrum. As it was assumed that the positron trapping rates due to dislocations and vacancies were the same, the positron lifetime spectrum never becomes single-component no matter how high the defect (dislocation and vacancy) concentrations are. Interestingly, although the “mean” positron lifetime was almost constant above a trapping rate of $10^{11}$ s$^{-1}$, as shown by the dashed line in the figure, $-\Delta T_0$ decreased.

Figure 7 shows the results of analysing the positron lifetime spectra obtained from the SUS304 samples after shot-peening. Herein, $-\Delta T_0$ is the shift from the $T_0$ value of the sample that was shot-peened for 0 s. Starting from 102.8 ps, the “mean” positron lifetime monotonically increased with the shot-peening time, reaching 169.9 ps at a time of around 240 s before becoming almost constant. Meanwhile, $-\Delta T_0$ increased between 0 and 36 s, then decreased between 36 and 1920 s. When the shot-peening time was more than 240 s, the “mean” positron lifetime was almost constant, but $-\Delta T_0$ monotonically decreased.

5. Discussion
Simple simulations and experiments using shot-peened samples showed that there is a $T_0$ shift $(\Delta T_0)$ in the analysis results when analysing multi-component positron lifetime spectra using an exponential function with a single-component. Therefore, to further examine the relation between $\Delta T_0$ and defect conditions, we created more realistic positron lifetime spectra via simulation and compared them with the experimental results.

5.1. Comparison of experimental and simulated results
The experimental positron lifetime spectra include a source component from the Kapton® enclosing the $^{22}$Na source. Therefore, we first assumed that the positron lifetime spectra included source components and involved three states, i.e., bulk, dislocations and vacancies, simulating them under the below conditions.

The positron lifetimes due to the bulk, dislocation, vacancy components, FWHM time resolution and channel width were the same as in the simulations in Fig. 4. We added a source component due to the $^{22}$Na enclosure (Kapton®) with a positron lifetime of 380 ps and 20% intensity. The total count was 1 M and the background was 10 counts/ch. Again, the trapping rates for dislocations and vacancies were the same, and we considered 12 rates ranging from $10^6$ to $10^{13}$ s$^{-1}$. We analysed the resulting positron lifetime spectra and computed the “mean” lifetime and $-\Delta T_0$ as a function of the trapping rate. The analyses were conducted under the same conditions as in the experiment shown in Fig. 7; except for the inclusion of the source component, whose lifetime and intensity were fixed at 380 ps and 20%.

Results of the above simulations are shown in Fig. 8, alongside the experimental results from Fig. 7. The lower horizontal axis shows the simulated trapping rate, whereas the upper axis shows the experimental shot-peening time. These have been scaled so that the variations in the “mean” positron lifetime for the experimental and simulated results are similar to each other. This figure shows 10 spectra with low trapping rates ($<10^{11}$ s$^{-1}$), taken from the 12 simulated spectra.

Figure 8 shows that the simulated results, despite being based on the simple assumption that the positron trapping rates due to dislocations and vacancies are the same, reproduced the changes in $-\Delta T_0$ obtained in the experiments. The peak $-\Delta T_0$ values were 15.5 ps and 9.9 ps in the simulations and experiments, respectively, but various factors can cause changes in $\Delta T_0$, just as it changed from 19.3 ps (Fig. 6) to 15.5 ps (Fig. 8) after the source component was added to the simulations. For this reason, a difference of a few picoseconds in the peak $\Delta T_0$ value is unlikely to represent an essential difference between the annihilation processes in the simulations and experiments.
error bars represent ±3

Herein, dislocations and vacancies) and the following equation assumed that the distribution was log-normal and obeyed the used to analyse the lifetime distribution width. This analysis obtained the corresponding lifetime distribution widths

\[ \Delta T_0 = \frac{1}{\sigma} \sigma x \exp \left( - \frac{(\ln x)^2}{2\sigma^2} \right), \quad 0 < x < \infty, \]

where \( f(x) \) is the lifetime distribution, \( x \) is the positron lifetime and \( \sigma \) is the lifetime distribution width. We analysed the lifetime spectra from the simulation shown in Fig. 6 and obtained the corresponding lifetime distribution widths (Fig. 10).

The lifetime distribution width monotonically increases with the trapping rate before decreasing again. The lifetime distribution width at a trapping rate of \( 10^{11} \text{s}^{-1} \) is approximately 0 ps and 27.8 ps for the two- and three-state model, respectively. However, it does not change much for trapping rates of more than \( 10^{11} \text{s}^{-1} \), whereas \( -\Delta T_0 \) decreases significantly (Fig. 6). Therefore, although the lifetime distribution width and \( \Delta T_0 \) are both parameters that reflect the positron lifetime spectrum’s complexity, their defect dependencies are essentially different.

Based on the three-state trapping model, for trapping rates of more than \( 10^{11} \text{s}^{-1} \), the dislocation and vacancy components of the positron lifetime spectra both exceed relative intensities of 49%. For this reason, the lifetime distribution width and “mean” positron lifetime do not change significantly for such trapping rates. On the contrary, the relative intensity of the bulk component (lifetime \( < 5 \text{ps} \)) decreases from 2.04% to 0.02% as the trapping rate increases from \( 10^{11} \) to \( 10^{13} \text{s}^{-1} \). Since \( \Delta T_0 \) is a parameter that expresses the starting time of the lifetime spectrum, where short lifetimes make large contributions, slight changes in the bulk component can have a significant impact.

Figure 11 plots the changes in the positron lifetime distribution widths of the SUS304 samples as a function of the shot-peening time, along with the “mean” positron lifetimes and \( -\Delta T_0 \) values (taken from Fig. 7). The lifetime

Figure 9 shows the relation between the “mean” positron lifetime and \( -\Delta T_0 \). The error bars represent three times the standard deviation \( (\pm 3\sigma) \) seen in the corresponding analyses (for a total of about 1 M counts). For “mean” positron lifetimes above 160 ps, we observe little change in the “mean” lifetime compared with the error bars, but significant changes are observed in \( -\Delta T_0 \). This suggests an effective use of \( \Delta T_0 \) in the evaluation of high defect concentrations with large trapping rates.

5.2. Comparison between the lifetime distribution width and \( \Delta T_0 \)

The positron lifetime spectrum of a metal is usually expressed as a sum of discrete lifetime components, but assuming a spectrum with a continuous positron lifetime distribution means the width of the distribution provides additional information about the positron annihilation process. When analysing positron lifetime spectra with multiple components using an exponential function with a single-component, \( \Delta T_0 \) reflects the difference between the actual and the fitted data, and can potentially show similar changes to those in the lifetime distribution width. We therefore compared the lifetime distribution width and \( \Delta T_0 \).

The IPALM by software included with the PSA system was used to analyse the lifetime distribution width. This analysis assumed that the distribution was log-normal and obeyed the following equation

\[ f(x) = \frac{1}{\sqrt{2\pi} \sigma x} \exp \left( - \frac{(\ln x)^2}{2\sigma^2} \right), \quad 0 < x < \infty, \]

where \( f(x) \) is the lifetime distribution, \( x \) is the positron lifetime and \( \sigma \) is the lifetime distribution width. We analysed the lifetime spectra from the simulation shown in Fig. 6 and obtained the corresponding lifetime distribution widths (Fig. 10).

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Fig. 9. (Color online) Relation between “mean” positron lifetime and \( \Delta T_0 \). Herein, ● are the simulated \( \Delta T_0 \) values for the three-state model (bulk, dislocations and vacancies) and ○ are the experimental \( \Delta T_0 \) values. The error bars represent \( \pm 3\sigma \) for a total of 1 M counts.

Fig. 10. (Color online) Variations in the lifetime distribution width for simulated positron lifetime spectra with different trapping rates. Herein, ◇ represent the simulations based on the two-state model (bulk and dislocations) and ● represent the simulations based on the three-state model (bulk, dislocations and vacancies).

Fig. 11. (Color online) Comparison of the positron lifetime distribution width with the “mean” positron lifetime and \( -\Delta T_0 \) (Fig. 7) for shot-peened SUS304. Based on the scaling of the horizontal axes in Fig. 8, shot-peening for about 800 s corresponds to a trapping rate of \( 10^{11} \text{s}^{-1} \) (dashed line).
distribution widths after shot-peening for 960 and 1920 s are approximately 33 ps. Based on the horizontal axis in Fig. 8, 800 s of shot-peening corresponds to a trapping rate of \(10^{11} \text{s}^{-1}\) (dashed line in Fig. 11). In the simulated positron lifetime spectra based on the two-state model (Fig. 10), the lifetime distribution width was 0 ps for trapping rates of \(10^{11} \text{s}^{-1}\) or higher. Therefore, the behaviour of the lifetime distribution width for shot-peened SUS304 is clearly different from that predicted by the two-state model simulation. In addition, \(-\Delta T_0\) decreases slightly for shot-peening times of approximately 800 s or more (dashed line in Fig. 11), indicating increased defect concentrations. It can therefore be concluded that, in SUS304 stainless steel with defects introduced by extended shot-peening, there are at least two types of defect (dislocations and vacancies), and their concentrations increase with the shot-peening time. In shot-peening, the aim is to introduce a sufficient concentration of dislocations, and \(\Delta T_0\) is useful for studying defects in shot-peened materials.

6. Conclusion

This research has found that \(\Delta T_0\) is a practically useful parameter, although it does not have a simple physical meaning. Similar to the lifetime distribution width, \(\Delta T_0\) reflects the complexity of the positron lifetime spectrum, but its defect dependency is different from that of the lifetime distribution width, and it is particularly useful for evaluating high defect concentrations.

In the positron annihilation lifetime measurement method, the suitable defect concentration range is said to be approximately 1–100 ppm, and defects with concentrations of 100 ppm or higher are understood to trap all the positrons (full trap). We found that \(\Delta T_0\) is sensitive to changes in the positron lifetime spectrum at high defect concentrations, where the “mean” positron lifetime becomes almost constant, and can be particularly useful for analysing defects in materials with defect concentrations of 100 ppm or higher. Based on the positron lifetime distribution widths and \(\Delta T_0\) values for SUS304 stainless steel after extended shot-peening, at least two types of defect were present, in increasing concentrations. In the future, we plan to consider using \(\Delta T_0\) for analysing defects in metals produced by fatigue tests and radiation.

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