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High-temperature In-situ Measurements of Thermal Vacancies in a TiAl Intermetallic Compound using a Desktop Positron Beam

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A desktop positron beam apparatus combined with a β^+-γ coincidence positron annihilation lifetime spectrometer was used for investigating thermal equilibrium vacancies in a TiAl intermetallic compound which is expected to find uses as a lightweight, heat-resistant structural material. The vacancy formation energy of the TiAl was derived from high-temperature in-situ measurements of positron lifetimes, and its value is in good agreement with a previously-reported value measured using a sophisticated internal positron source method. The measurement method used in this study makes it possible to investigate the vacancy formation energies in any material at high temperatures easily, even in unweldable ceramics, semiconductors, and brittle intermetallics for which conventional internal positron source methods cannot be applied.

1. Introduction

To understand the migration of substitutional atoms in crystalline materials, the vacancy mechanism [1] is considered to be a dominant process since the activation energy is minimal compared to a direct exchange mechanism or a ring mechanism. The migration rate of the substitutional atoms is proportional to the probability that the vacancy exists at the adjacent site of the substitutional atom, *i.e.*, the migration rate is proportional to the vacancy concentration in crystals. On the other hand, owing to the entropy of arrangement of atoms and vacancies, crystals contain vacancies in order to minimize the free energy, except at absolute zero temperature. Such vacancies are called thermal equilibrium vacancies, and those concentrations are exponentially affected by temperature and the vacancy formation energy. Thus, investigating vacancy formation energies is an important research topic for understanding various phenomena accompanying atomic migration/diffusion. Vacancy formation energies in crystalline materials can be obtained by measuring the temperature dependence of the thermal equilibrium vacancy concentration [2, 3].

Nowadays, positron annihilation spectroscopy is widely used for investigating vacancies. Positron lifetimes are usually measured by the so-called sandwich method using a ^{22}Na sealed positron source. However, heating the sample together with the sealed positron source in order to measure the thermal equilibrium vacancies at high temperatures involves a risk of radioactive leaks. Therefore, conventionally, high-temperature in-situ measurements of thermal equilibrium vacancies with positron annihilation lifetime spectroscopy have used either the monoenergetic positron beam method (moderated positrons are re-accelerated to MeV energy) [4, 5] or the internal positron source method (embedding a positron source inside a sample and sealing the source by electron-beam welding) [3]. However, both methods have disadvantages such as the large size of the experimental apparatus (monoenergetic positron beam method) or difficulty in sample preparation (internal positron source method). Shirai and co-workers proposed a third method in which fast positrons emitted from a ^{68}Ge sealed positron source are directly irradiated into a sample at high temperatures with magnetic lenses to eliminate low-energy positrons which cause a degradation of the time resolution in positron lifetime measurements [6–9]. This third method allows us to separate the positron source from the heated sample like in the monoenergetic positron beam method. Further, a practical counting rate can be obtained even with a relatively weak positron source since positron moderation is not necessary. In this study, thermal equilibrium vacancies in an $L1_0$-type TiAl intermetallic compound were investigated using a desktop positron beam apparatus based on the third method [9]. TiAl has light-weight and high-strength, and excellent oxidation resistance. Thus, this material is used for automobile turbochargers or aerospace engines [10–13]. Since the vacancy concentration affects the creep behavior of materials, investigating the vacancy formation energy is important also for the structural materials used at high temperatures. The vacancy formation energy in TiAl was previously reported to be 1.41 eV [3] by applying a sophisticated internal positron source method [14]. We conducted a measurement to derive the vacancy formation energy of TiAl using a desktop positron beam apparatus and compared it with the previously-reported value.

2. Experiment

TiAl samples were prepared by the following procedure. A $Ti_{48}Al_{52}$ ingot was made by arc-melting from Ti (99.5 %) and Al (99.999 %) in Ar atmosphere. The ingot was then subjected to homogenizing heat treatment at 1473 K for 8 days in Ar atmosphere. The homogenized ingot was cut out in two semicircular disks with a radius of 17 mm and a thickness of 1.5 mm using a wire electrical discharge machine. The two semicircular disks were subjected to mechanical and chemical polishing. Finally, the two semicircular disks were loaded into the desktop positron beam apparatus as a single circular-disk-shape sample and annealed at 1473 K for 12 hours in vacuum to eliminate lattice defects. Another set of square samples with a size of $(10 \times 10 \times 1.5)$ mm^3 were cut out for a conventional γ-γ positron annihilation lifetime measurement from the same homogenized ingot. The square samples were also subjected to annealing at the same conditions.

The desktop positron beam apparatus used in this study consists of a 3.7 MBq ^{68}Ge positron source for obtaining high-energy positrons, an avalanche photo-diode (APD) for detecting positron emission timing [15], and a permanent magnetic lens for eliminating low-energy positrons. The sample was loaded in the center of a cylindrical vacuum chamber with a diameter of 300 mm and a height of 300 mm. The ^{68}Ge positron source was installed 200 mm above the heating sample to protect it from thermal damage. High-energy positrons after passing through the APD are focused and irradiated into the sample. As low-energy positrons cause wide time-of-flight dispersion [9], the low-energy positrons less than 200 keV were eliminated by the magnetic lens largely refracting outwards from the axis. Such low-energy positrons annihilate on the inner wall of the vacuum chamber and their annihilation gamma-rays are hardly detected by the stop detector (a photomultiplier tube coupled with a BaF_2 scintillator) installed on the backside of the sample. The elimination of low-energy positrons makes it possible to separate the positron source from the heated sample without degrading the time resolution in the positron lifetime measurement. For the sample heating, an electron-bombardment heating system [9, 16] was adopted, and a few kV was applied to the sample in order to accelerate thermoelectrons emitted from a tungsten filament. The details of the apparatus are described elsewhere [9]. By using this desktop positron beam apparatus combined with the β^+-γ coincidence positron annihilation lifetime spectrometer, high-temperature in-situ measurements of positron lifetimes in the TiAl sample were conducted with a counting rate of a few hundred per second, and approximately 1×10^6 total events were accumulated for each lifetime spectrum. In-situ positron annihilation lifetime measurements were conducted during the heating process from room temperature to 1273 K. The measurements were also performed at several temperatures during the cooling process. The obtained lifetime spectra were analyzed using the PATFIT-88/POSITRONFIT program [17, 18].

3. Results and discussion

The positron lifetime was also measured at room temperature using a conventional γ-γ method with a time resolution of 179 ps full width at half-maximum (FWHM). A single lifetime component of 144.7 ps was found, which is almost the same value as the positron lifetime of an annealed $Ti_{48.5}Al_{51.5}$ alloy (143 ps) reported in a previous study [3]. In TiAl intermetallic compounds, no structural vacancies are reported to be formed around this stoichiometric composition [19]. Indeed, no positron lifetime component corresponding to structural vacancies was observed in the $Ti_{48}Al_{52}$ alloy used in this study. Figure 1 shows a lifetime spectrum of the TiAl sample measured at room temperature by the desktop positron beam apparatus combined with the β^+-γ coincidence positron annihilation lifetime spectrometer. Positron lifetime components of 144.4 ps (93 %) and 767.2 ps (7 %) were detected with a time resolution of 309 ps FWHM. Most of the longer lifetime component is considered to be derived from positrons annihilated in the upper end of the cylindrical ceramic sample holder (36 mmϕ×34 mmϕ×30 mmH), and it has been confirmed the component does not change largely even when heating the sample. Thus, the longer lifetime obtained here was assigned to an equipment component. Although the time resolution is not as good compared with the conventional γ-γ method, the measured lifetime component of 144.4 ps was almost the same (144.7 ps). In this study, all positron annihilation lifetime spectra measured at high-temperatures were analyzed by subtracting the lifetime component of 767.2 ps (7 %) as an equipment-inherent component.

Figure 2 shows the temperature dependence of mean positron lifetime of the TiAl sample. The mean positron lifetime shows a reversible change in heating and cooling processes, which means a reversible thermal equilibrium change. Below 1000 K, a moderate increase of mean positron lifetime, corresponding to the thermal expansion of TiAl crystalline lattice, is observed. No significant increase of the variance of the fit ((χ^2/q), shown in the upper part of Fig. 2) is observed in this temperature

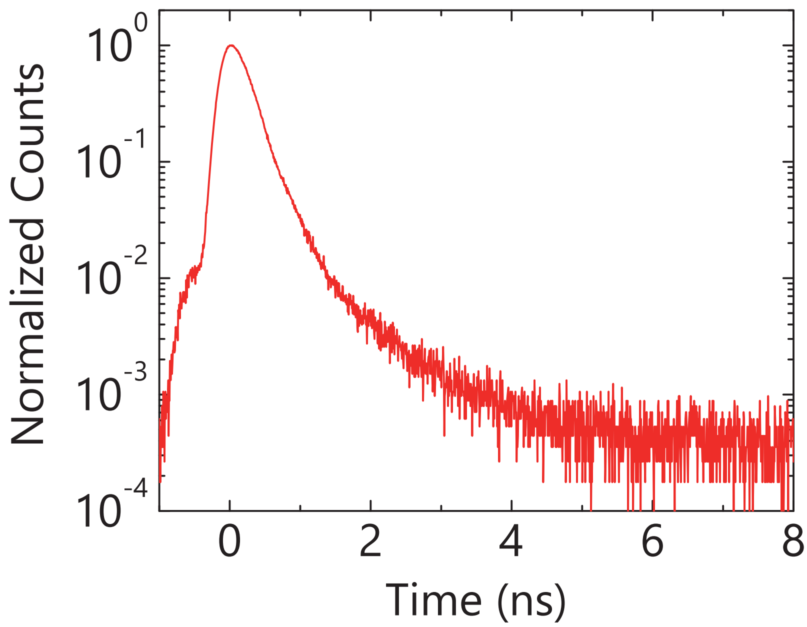

Fig. 1 Positron annihilation lifetime spectrum for a TiAl sample measured at room temperature by the desktop positron beam apparatus.

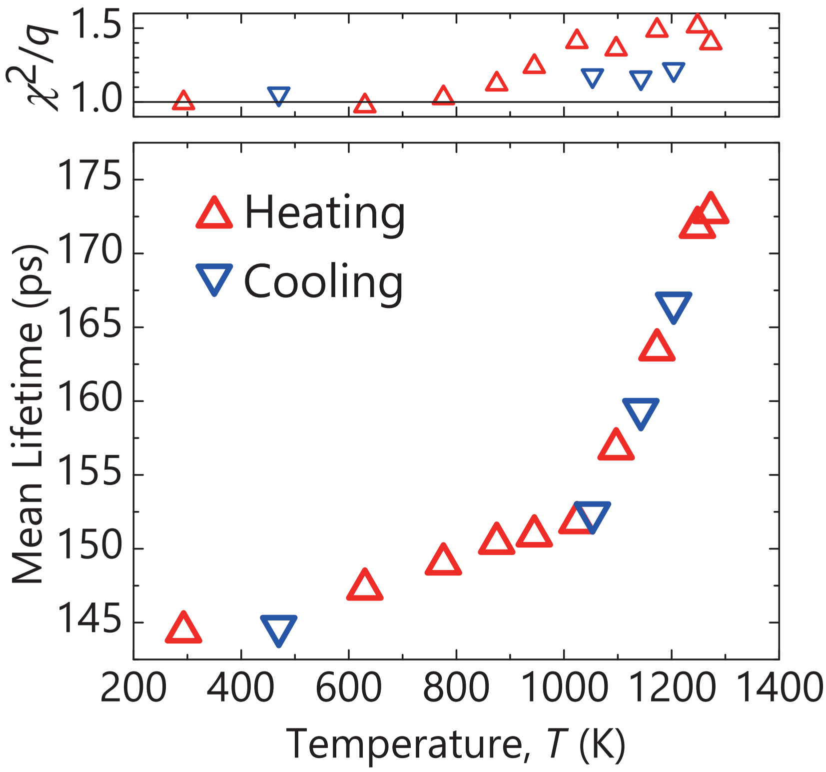

Fig. 2 Temperature dependence of mean positron lifetime of a TiAl sample. Symbols in red open upper triangular and blue open lower triangular are measured points during heating and cooling, respectively. The variance of the fit (χ^2/q) for the single component analysis is also shown in the upper part of the figure.

range. This indicates each positron lifetime spectrum is well fitted with single lifetime component shown as the mean positron lifetime without a vacancy component. In contrast, a drastic increase of mean positron lifetimes is obtained above 1000 K, and an increase in the value of the χ^2/q is also seen. This indicates the formation of thermal equilibrium vacancies in the TiAl sample. A two-component analysis of the lifetime spectra acquired at 1097 K and higher was carried out.

Based on the two-state trapping model [2,20,21], the positron annihilation lifetime spectrum $L(t)$ is expressed by the following equations:

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

$$\tau_0 = (\lambda_f + \kappa)^{-1} \quad (2)$$

$$\tau_d = \lambda_d^{-1} \quad (3)$$

$$I_0 = (\lambda_f - \lambda_d)/(\lambda_f + \kappa - \lambda_d) \quad (4)$$

$$I_d = \kappa/(\lambda_f + \kappa - \lambda_d) \quad (5)$$

where λ_f and λ_d are the positron annihilation rates in the free-state and in the defect, I_0 and I_d are the relative intensities of τ_0 and τ_d components, κ is the positron trapping rate. The total relative intensity of the two components is unity ($I_0 + I_d = 1$). From the equations, the positron trapping rate κ is given by the following equation:

$$\kappa = I_d(\tau_0^{-1} - \tau_d^{-1}) \quad (6)$$

Positron lifetime spectra measured at 1097 K–1273 K were decomposed into two exponential terms shown in equation (1) after background and equipment-inherent component corrections as shown in

Fig. 3. As the result of the two-component analysis, the values of χ^2/q are close to unity, which means that each positron annihilation lifetime spectrum is well fitted with the two lifetime components shown in Fig. 3. The positron lifetime in the free-state τ_f $(= \lambda_f^{-1})$ is known as 144.4 ps from the measurement at room temperature shown in Fig. 1, and the positron trapping rate κ at each temperature is given from the result of two-component analysis shown in Fig. 3. Therefore, τ_0 can be calculated as τ_0^{TM} by Eq. (2). The calculated τ_0^{TM}s are also shown in Fig. 3, and the agreement of τ_0 and τ_0^{TM} confirms the validity of the analysis based on the two-state trapping model. The result of the two-component analysis shows I_d increases with increasing temperature although τ_d is constant. This shows that the concentration of thermal equilibrium vacancies increases with increasing temperature.

From the thermodynamic theory of point defects, the vacancy concentration C_V is given by the following equation as a function of temperature T [22]:

$$C_V = \exp(S_V^F/k_B)\exp(-H_V^F/k_BT) \tag{7}$$

where S_V^F, H_V^F, and k_B are the vacancy formation entropy, the vacancy formation energy, and the Boltzmann constant, respectively. Since the product of the vacancy concentration C_V and the specific positron trapping rate ν is the positron trapping rate κ $(\nu C_V = \kappa)$, Eq. (7) can be written as follows:

$$\begin{aligned}\kappa &= \nu\exp(S_V^F/k_B)\exp(-H_V^F/k_BT)\\ &= A\exp(-H_V^F/k_BT)\end{aligned}$$

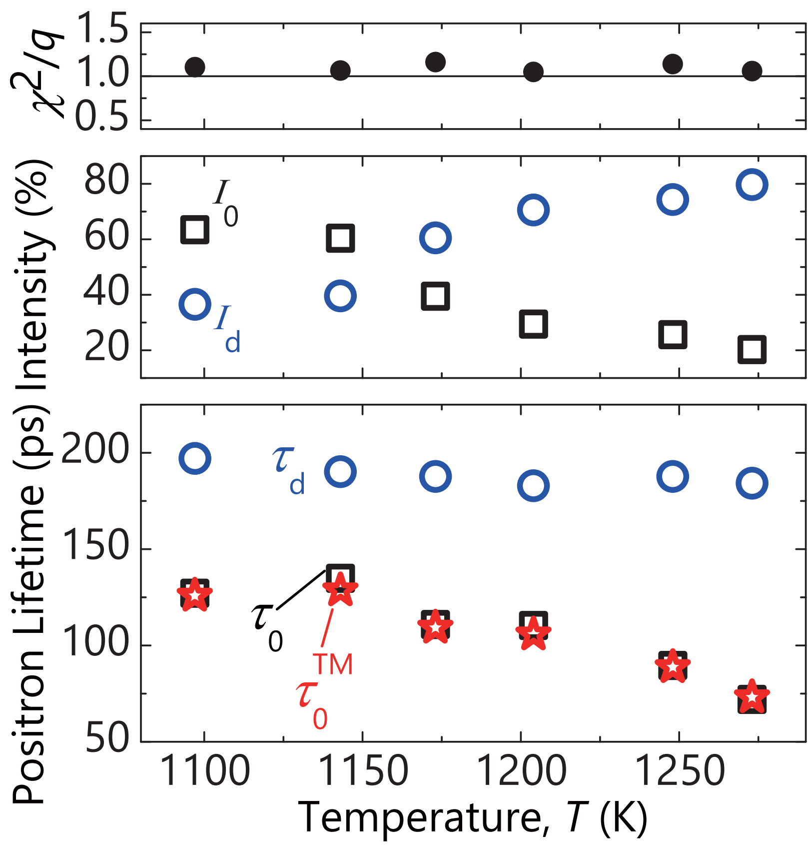

Fig. 3 Temperature dependence of positron lifetimes (τ_0, τ_d) and their intensities (I_0, I_d) in the temperature range from 1097 K to 1273 K. The calculated lifetimes τ_0^{TM} based on the two-state trapping model are also shown by red open stars.

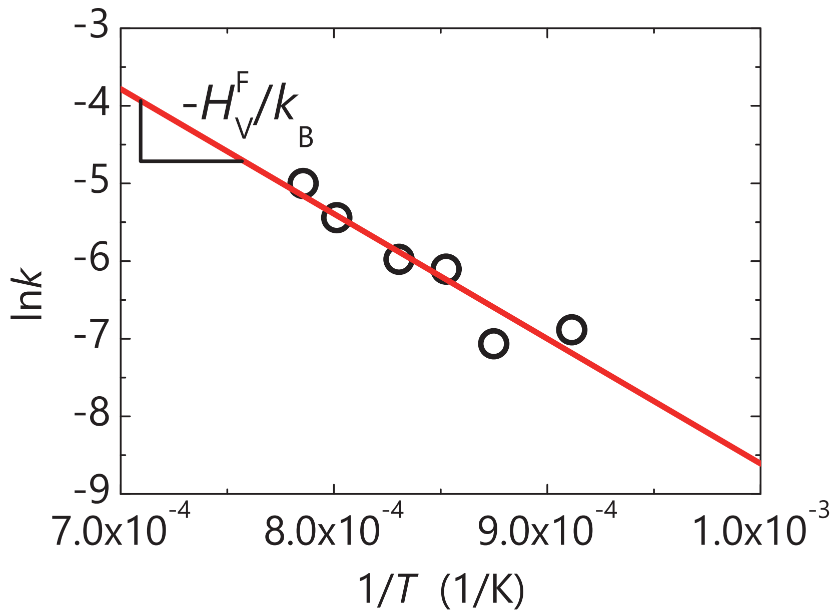

Fig. 4 Arrhenius plot of the positron trapping rate κ of a TiAl sample in a temperature range from 1097 K to 1273 K.

$$\ln\kappa = \ln A - (H_V^F/k_B)(1/T) \tag{8}$$

where A is constant. The Arrhenius plot of the positron trapping rate κ shown in Fig. 4 can be obtained from the result of the two-component analysis shown in Fig. 3 and equation (6). From Eq. (8), the Arrhenius plot gives $-H_V^F/k_B$ as the slope of the straight line. Therefore, the vacancy formation energy H_V^F can be derived from the high-temperature in-situ measurements of positron lifetimes. The H_V^F of the TiAl sample obtained in this study was 1.39 eV, in good agreement with the previously-reported value (1.41 eV) measured using the sophisticated internal positron source method [3]. As described above, the desktop positron beam apparatus enables the measurement of the vacancy formation energy more easily than the monoenergetic positron beam method or the internal positron source method. It is noteworthy that the measurement method used in this study makes it possible to measure positron lifetimes at high temperatures even for unweldable materials to which the internal positron source method cannot be applied. The vacancy formation energies of hard-to-weld materials such as ceramics, semiconductors, and a large majority of intermetallics have not been investigated sufficiently, and the desktop positron beam apparatus is expected to become a powerful tool for such studies.

4. Summary

High-temperature in-situ positron annihilation lifetime measurements of a TiAl intermetallic compound were conducted using a desktop positron beam apparatus combined with a β^+-γ coincidence positron annihilation lifetime spectrometer. From the measured positron lifetime, the vacancy formation energy of the TiAl sample was derived to be 1.39 eV, in good agreement with a previously-reported value measured using the internal positron source method. The desktop positron beam apparatus allows us to investigate vacancy formation energies conveniently with a relatively weak positron source, and is expected to become a powerful tool for investigating unweldable materials to which the conventional internal positron source method cannot be applied.

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