Anomalous Temperature Changes of Positron Lifetime and Electrical Resistivity in B2-NiTi Alloys

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The pre-martensitic phenomena in Ni-rich NiTi alloys have been studied by means of positron lifetime spectroscopy and electrical resistivity measurement. We have found anomalous positron lifetime changes above the martensitic transformation temperatures of Ni50Ti50–Ni53Ti47 alloys. Almost the same change in positron lifetime has been observed on the subsequent heating run with little hysteresis. We have also found the anomalous behavior of positron lifetime and negative temperature dependence of electrical resistivity even in NiTi alloys that do not exhibit martensitic transformation. The observed pre-martensitic changes of positron lifetime and electrical resistivity directly reflect the intrinsic electronic-structural changes of NiTi alloys that cause so-called pre-martensitic phenomena.

(Received June 3, 2002; Accepted June 12, 2002)

Keywords: nickel titanium alloy, martensitic transformation, positron lifetime, electrical resistivity, electronic structure

1. Introduction

The shape memory effect is now a well-known phenomenon associated with reversible martensitic transformation, which is a typical displacive transition. The effect has been discovered in many materials, such as Ni–Ti, Cu–Al–Ni, Cu–Zn, Fe–Mn–Si and Fe–Ni–Co–Ti alloys, and has been a matter of interest in both theoreticians and practice with respect to smart materials. In particular, near-equiaxial NiTi alloys are extensively used in consumer appliances such as eyeglass frames, antennae for portable telephones and mixing valves in water pipes. Many investigations have therefore been made into the transformation process of the alloys using various experimental techniques.1–12)

In recent years, anomalous phenomena have been observed above the martensite start (Ms) temperature, such as a negative temperature coefficient of electrical resistivity,1–7) decrease of sound velocity,3,8) increase of internal friction,9,10) softening of elastic shear constants,11) and superlattice reflections of 1/3(110) and 1/3(111) types in electron and X-ray diffraction patterns.5,12,13) These phenomena have attracted much attention in relation to the precursor of the martensitic transformation. The large majority of pre-martensitic phenomena have been observed in phonons, and little information has been obtained concerning the change in the electron system of the parent phase prior to the martensitic transformation, which should be the origin of all pre-martensitic phenomena. In the previous paper,14) we reported an anomalous change of the electronic structure in the parent phase (B2) before transformation to the martensitic phase (B19′) in Ni53Ti47 alloy, observed by means of positron lifetime measurement.

Positron lifetime directly reflects the electronic structure, because positron lifetime is inversely proportional to the electron density at the annihilation site. Brandt et al.15) indicated the relationship between positron lifetime, $\tau_B$, and electron density, $n_0$ (a.u.), for metal bulk as

$$\tau_B = 1/(2 + 134n_0) \times 10^3 \text{ (ps)} \quad (1)$$

On the other hand, if there exist vacancy-type defects, such as vacancies, voids and dislocations in a specimen, the positron lifetime is not determined by the bulk electronic property, since positrons are sensitively trapped in such defects and annihilate with the characteristics of each type of defect. Thus, the measurement of positron lifetime also serves as a good tool for detecting crystal lattice defects in metals.16)

The martensitic transformation behavior of NiTi alloys is well known to depend on their composition, heat treatment and thermal cycling.4,17) For example, the increase of Ni concentration from 50 to 51 at% causes a large decrease, about 100 K, in the Ms temperature. In order to eliminate unexpected differences in transformation temperature among different specimens, it is desirable to measure the positron lifetime simultaneously with monitoring of the martensitic transformation behavior of the same specimen by other measuring method. We have, therefore, measured the positron lifetime spectra and electrical resistivity at the same time in order to clarify the electronic structure change before and after the thermoelastic martensitic transformation on near-equiaxial NiTi alloys.

2. Experimental Procedure

Ni100–xTi x (x = 50, 49.5, 49, 48, 47, 46) alloy ingots were prepared by repeated arc-melting of pure nickel (99.97%) and sponge titanium (99.875%) in high-purity argon atmosphere. They were annealed for 180 ks at 1273 K in argon atmosphere for homogenization, and subsequently quenched in iced water. The alloy samples were cut into 10×10×1.5 mm3 plates using a spark cutting machine and were electrolytically polished.

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For each sample, the positron lifetime spectrum and electrical resistivity were simultaneously measured at temperatures between 125 and 335 K. Positron lifetime measurements were made using a fast-fast timing coincidence system with a time resolution of 190 ps (FWHM). A positron source of $^{22}\text{NaCl}$ (1 MBq) was sandwiched between two identical sample plates. The source correction and the resolution functions were evaluated using the code RESOLUTION. The lifetime spectra were analyzed using the POSITRONFIT EXTENDED program. Electrical resistivity measurements were carried out for one of the two sample plates by the four-probe method.

The differential scanning calorimetry (DSC) measurements were also carried out in the temperature range between 150 and 350 K for samples cut from the same ingots as were samples for positron lifetime and electrical resistivity measurements, in order to determine the transformation temperatures. The cooling and heating rates were 10 K/min.

3. Results and Discussion

Figure 1 shows the DSC thermograms for Ni51Ti49 and Ni52Ti48 alloys quenched into iced water after solution treatment at 1273 K. The virgin samples which had never undergone transformation to martensite were first cooled from 350 to 150 K, and then finally heated to 350 K. For Ni51Ti49 alloy, a single heat-flow peak is observed in the cooling and heating processes, as shown in Fig. 1(a). The DSC curves of Ni50Ti50 and Ni50.5Ti49.5 alloys also have single peaks, and are quite similar to that of Ni51Ti49 alloy. These single exothermic and endothermic peaks indicate that the direct martensitic transformation from the B2 to B19′ phase and the reverse transformation from the B19′ to B2 phase take place in these alloys. The transformation temperatures determined from the DSC curves are shown in Table 1. The martensitic reaction exhibits a hysteresis of about 30 K in each NiTi alloy. On the other hand, no heat-flow peaks are observed in the DSC curves of Ni52Ti48, Ni53Ti47 and Ni54Ti46 alloys. As an example, the DSC curve of Ni53Ti48 alloy is shown in Fig. 1(b). These observations reveal that these alloys do not exhibit the martensitic transformation in the temperature range of measurement. This result agrees with those of past investigations by X-ray and DSC measurements, which showed that NiTi alloy does not transform from the B2 to B19′ phase even at 90 K if the Ni content becomes no less than 52 at%.

Figure 2 shows the temperature change of positron mean lifetime $\tau_m$, during the first martensitic transformation and subsequent reverse transformation of a virgin Ni51Ti49 alloy. The figure also shows the electrical resistivity change measured for the same specimen at the same time as the positron lifetime measurement. The electrical resistivity exhibits similar behavior to that observed in the previous investigations. It has been shown experimentally that electrical resistivity starts to decrease at the $M_s$ temperature. Martensitic transformation from the B2 to B19′ phase occurs at 218 K in this alloy. The other transformation temperatures ($M_f$, $A_s$ and $A_f$) of the alloy determined by this measurement are indicated in Fig. 2 by arrows: they agree with the values measured by DSC (Table 1).

Positron mean lifetime at room temperature is much shorter than that in a vacancy, $\tau_v = 197$ ps, and is even shorter than that in the free positron state, $\tau_f = 132$ ps, for the Ni51.7Ti48.3 alloy with the B2 structure reported by Wuerschum et al. It is obvious that the majority of positrons are not trapped in any lattice defects. In other words, non-stoichiometry in

![Figure 1](image1)

**Fig. 1** DSC curves of (a) Ni51Ti49 and (b) Ni52Ti48 alloys quenched from 1273 K.

<table>
<thead>
<tr>
<th></th>
<th>$M_s$ (K)</th>
<th>$M_f$ (K)</th>
<th>$A_s$ (K)</th>
<th>$A_f$ (K)</th>
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<td>Ni50Ti50</td>
<td>316</td>
<td>301</td>
<td>329</td>
<td>349</td>
</tr>
<tr>
<td>Ni50.5Ti49.5</td>
<td>293</td>
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<td>301</td>
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<tr>
<td>Ni51Ti49</td>
<td>220</td>
<td>190</td>
<td>227</td>
<td>253</td>
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Table 1 Transformation temperatures for NiTi alloys measured by DSC.

![Figure 2](image2)

**Fig. 2** Temperature dependence of positron mean lifetime $\tau_m$, variance of the fit for the analysis of positron lifetime spectra $\chi^2/q$, and electrical resistivity in Ni51Ti49 alloy quenched from 1273 K.
Ni_{51}Ti_{49} alloy is primarily compensated with anti-site atoms. This conclusion supports the interpretation of Kato et al.\(^\text{23}\) As temperature is lowered from 325 to 220 K, \(\tau_m\) continuously increases from 120 to 150 ps, and then begins to decrease when the temperature is lowered further from 220 K. The \(\tau_m\) curve for heating almost falls on that for cooling, and the hysteresis of \(\tau_m\) is very small, although it is about 30 K as evaluated from the DSC thermogram and electrical resistivity change. Normally, the electron density in metals decreases with increasing temperature on account of thermal expansion, and equation (1) requires that positron lifetime generally decreases with lowering temperature. However, the \(\tau_m\) of Ni_{51}Ti_{49} alloy shows an anomalous increase with lowering temperature from 325 K to the \(M_s\) temperature of 220 K. The value of \(\chi^2/q\) is very close to unity, as shown in Fig. 2, which suggests that there is almost only one kind of positron annihilation site in the specimen at each temperature.

Figures 3 and 4 show the temperature dependences of \(\tau_m\) and electrical resistivity of Ni_{50}Ti_{50} and Ni_{50.5}Ti_{49.5} alloys. The transformation temperatures of the alloys determined by the electrical resistivity measurements agree with the values obtained by DSC (Table 1). It is noteworthy that, at 335 K where these alloys have the B2 structure, \(\tau_m\) is much longer than 120 ps. \(\tau_m\) of Ni_{51}Ti_{49} alloy is 120 ps at temperatures above 313 K where \(\tau_m\) has not yet started to anomalously increase with lowering temperature, and therefore the value of 120 ps is regarded as the “normal” positron mean lifetime in the free state for Ni_{51}Ti_{49} alloy. It is indicated that the anomalous increase of \(\tau_m\) with lowering temperature also takes place in Ni_{50}Ti_{50} and Ni_{50.5}Ti_{49.5} alloys. Differences between the behavior of Ni_{51}Ti_{49} alloy and those of Ni_{50}Ti_{50} and Ni_{50.5}Ti_{49.5} alloys are considered to be related to their transformation temperatures. Measurements at temperatures higher than 335 K are now in progress.

The difference in the crystal structures of B2 and B19’ may produce considerable difference in \(\tau_m\). However, the static change of the crystal structure cannot explain such anomalously long \(\tau_m\). For Ni_{51}Ti_{49} alloy, the temperature at which \(\tau_m\) begins to increase with lowering temperature is about 100 degrees higher than the \(M_s\) temperature. This anomalous increase of \(\tau_m\) implies that the electron density in the interstices of the B2 lattice becomes lower and seems to approach that of B19’ as the temperature approaches the \(M_s\) temperature. This result is consistent with the anomalous increase of electrical resistivity above the \(M_s\) temperature,\(^{1–6}\) since the electrical resistivity should increase with the decrease of conduction electron density. The electronic-structural change is probably related to the instability of the B2 phase, which gives rise to so-called pre-martensitic phenomena.

Figure 5 shows the changes of \(\tau_m\) and electrical resistivity of Ni_{51}Ti_{49} alloy. Electrical resistivity continuously increases with lowering temperature with no hysteresis, so-called negative temperature dependence, as reported by Fukuda et al.\(^{7}\) This result indicates that the alloy does not exhibit martensitic transformation within the temperature range. \(\tau_m\) increases with lowering temperature from 335 to 200 K, and then stops increasing at about 200 K, in contrast to the electrical resistivity, and has little hysteresis. The majority of positrons annihilate at one kind of annihilation site since \(\chi^2/q\) values are almost unity. The maximum value of \(\tau_m\) is much shorter than...
that for vacancies.\(^{21,22}\) The anomalous increase of \(\tau_m\) from 125 to 150 ps caused by the decrease in temperature from 335 to 200 K is quite similar to the increase of \(\tau_m\) observed above the \(M_s\) temperature in Ni\(_{52}\)Ti\(_{48}\) alloy (Fig. 2). The simple estimation based on the eq. (1) indicates about 20% decrease in \(n_0\). This change cannot be ascribed to the volume expansion, since the volume of B2 lattice decreases with lowering temperature. Consequently, we cannot but take the electronic-structural change into consideration. The anomalous increase of \(\tau_m\), specifically, indicates that the electron density at the positron annihilation site becomes significantly lower as the temperature is lowered.

Figure 6 shows changes of electrical resistivity and mean positron lifetime for Ni\(_{53}\)Ti\(_{47}\) and Ni\(_{54}\)Ti\(_{46}\) alloys which do not exhibit the martensitic transformation. The results for Ni\(_{52}\)Ti\(_{48}\) alloy shown in Fig. 5 are also plotted in Fig. 6 for comparison. Electrical resistivity shows a continuous increase with lowering temperature. This result indicates that the specimens do not transform. On the other hand, \(\tau_m\) increases with lowering temperature but stops increasing when the value reaches 150 ps. These behaviors of electrical resistivity and \(\tau_m\) are almost similar to those of Ni\(_{52}\)Ti\(_{48}\) alloy, although the rates of change decrease with Ni content. The density of conduction electrons at room temperature seems to decrease with Ni content, and this tendency is consistent with the increase of \(\tau_m\) at room temperature.

More detailed studies on other alloys and in wider temperature ranges are now in progress.

4. Conclusions

The positron lifetime and electrical resistivity measurements of Ni\(_{100-x}\)Ti\(_x\) (\(x = 50, 49.5, 49, 48, 47, 46\)) alloys were carried out at temperatures between 125 and 335 K. Above the \(M_s\) temperature, the mean positron lifetime, \(\tau_m\), increases anomalously with lowering temperature in the alloys, and the change is reversible with temperature. Negative temperature changes are observed even for the alloys which do not exhibit the martensitic transformation. The anomalous change of \(\tau_m\) reflects the intrinsic electronic-structural change of the B2 phase.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and in part by the Light Metal Educational Foundation Inc. This work was partly carried out at the Strategic Research Base “Handai Frontier Research Center” supported by the Japanese Government’s Special Coordination Fund for Promoting Science and Technology.

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