Pre-martensitic phenomena of thermoelastic martensitic transformation of NiTiCu alloys studied with positron annihilation lifetime spectroscopy

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Abstract

Many anomalous phenomena have been observed in NiTi alloys above martensite start temperature, such as softening of the shear constants, increase of internal friction and diffuse scattering of TEM. However, little information has been obtained about 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 this work, the temperature change of positron annihilation lifetime, which is quite sensitive to electronic-structural changes of matter, were carried out for NiTiCu alloys. The alloys show martensitic transformation from a B2 (cubic) phase to a B19' (monoclinic) phase via a B19 (orthorhombic) phase as the temperature is lowered. We have found anomalous positron lifetime changes in Ni10Ti50Cu40 and Ni15Ti50Cu35 alloys which show a B2–B19–B19’ phase transformation. Positron lifetime increases anomalously with decreasing temperature at temperatures higher than the transformation temperature into a B19’ phase. On the other hand, positron lifetime does not show any anomaly in the B2 phase of Ni30Ti50Cu20 alloy which shows B2–B19 phase transformation. The positron lifetime of the parent B2 phase shows good agreement with the theoretically-calculated value. Those of the martensite phases of B19 and B19’, although, are about 30 ps longer than calculated ones. This big difference between experimental and calculated positron lifetimes cannot be explained by any existing theory.

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1. Introduction

The shape memory effect is now a well-known phenomenon associated with thermoelastic martensitic transformations. The effect has been discovered in many materials, such as NiTi-, Cu- and Fe-based alloys with typical thermoelastic martensitic transformations and has been a matter of interest in both theoretics and practice. The NiTi alloy, among them, is most important due to the excellent mechanical properties.

Many anomalous phenomena have been observed in NiTi alloys above martensite start temperature, such as softening of the shear constants [1], increase of internal friction [2] and diffuse scattering of neutron inelastic scattering and TEM [3,4]. However, little information has been obtained about 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.

We reported an anomalous behavior of electronic-structure change in the region of B2 parent phase before transforming into a B19’ martensitic phase in Ni51Ti49 alloy observed by positron lifetime measurement in a previous paper [5]. We also found similar behavior of positron lifetime even in NiTi alloy which does not exhibit the martensitic transformation [6]. However, the origin of pre-martensitic phenomena in NiTi alloys has not been clarified yet.

Near-equatomic binary NiTi alloys quenched from a solution treatment temperature show the direct martensitic transformation from a B2 (cubic) phase to a B19’ (monoclinic) martensitic phase. On the other hand, it is well known that NiTiCu alloys (some Ni is substituted by Cu) show two-stage martensitic transformation, from a B2 phase to a B19’ phase via B19 (orthorhombic) intermediate martensitic phase, as the temperature is lowered.

In this work, in order to clarify the origin of anomalous behavior of positron lifetime as observed in NiTi alloy, positron lifetime spectra and electrical resistivity were measured for the NiTiCu alloys which have different martensitic transformation paths from binary NiTi alloys.
Positron lifetimes were calculated by using the first-principle calculation and compared with the experimental results.

2. Experimental procedure

Ni_{51}Ti_{49}, Ni_{40}Ti_{50}Cu_{10}, Ni_{35}Ti_{50}Cu_{15} and Ni_{30}Ti_{50}Cu_{20} alloy ingots were prepared by repeated arc melting of Ni (99.97%), Ti (99.875%) and Cu (99.99%) in high purity argon atmosphere. They were annealed for 180 ks at 1273 K in argon atmosphere for homogenization. The samples were cut into 10 x 10 x 1.5 mm\(^3\) plates with a spark cutting-machining and annealed for 7.2 ks at 1273 K (1323 K for NiTiCu alloys), and subsequently quenched in iced water and electrolytically polished.

Positron lifetime spectrum and electrical resistivity were simultaneously measured for the samples at temperatures between 100 and 400 K. Positron lifetime measurements were carried out by using a fast–fast timing coincidence system with a time resolution of 190 ps (FWHM). A positron source of \(^{22}\)NaCl (1 MBq) was sandwiched between two identical sample plates. The lifetime spectra were analyzed by using codes RESOLUTION [7] and POSITRONFIT EXTENDED [8,9]. Electrical resistivity measurements were carried out for one of the two sample plates by using the four-probe method.

3. Positron lifetime calculation

Positron annihilation lifetime can be calculated by using first principle theory. We compare calculated positron lifetimes to experimental ones and discuss about the anomalous behavior of the positron lifetime in NiTi alloys. The electronic structures of B2, B19 and B19\(^0\) phases of NiTi alloys are calculated by the DV-X\(\alpha\) cluster method which is one of the first principle molecular orbital methods employing a Slater’s X\(\alpha\) exchange-correlation potential. The detailed explanation of this calculation method is given elsewhere [10]. The Schrödinger equation for the positron is solved by the finite-difference method [11] employing the periodic boundary conditions for delocalized positron wave function in the bulk state. The positron annihilation rate \(\lambda\), which is the inverse of the positron lifetime \(\tau\), is calculated from the overlap of the positron and electron densities as

\[
\lambda = \pi r_e^2 c \int n_-(r)n_+(r)\gamma(r)d^3r
\]  

(1)

where \(r_e\) is the classical electron radius \((r_e = [3/(4\pi n_-)]^{1/3})\) provided by Borowski et al. [12], \(c\) is the speed of light. The electron \(n_-(r)\) and positron \(n_+(r)\) densities are determined self-consistently by using the two-component density-functional formalism [12]. \(\gamma(r)\) is the enhancement factor which shows the screening effect on the positron by electron cloud and the value fitted by Puska et al. [13] based on the data by Lantto [14] is applied in this work.

4. Results and discussion

Fig. 1 shows temperature dependence of positron mean lifetime \(\tau_m\) on the first martensitic transformation and subsequent reverse transformation of a virgin Ni_{51}Ti_{49} alloy. The figure also shows an electrical resistivity change measured for the same specimen at the same time with the positron lifetime measurement. The electrical resistivity exhibits similar behavior observed in the previous investigations [15–17]. It has been shown experimentally that electrical resistivity starts to decrease at the \(M_s\) temperature [16]. The resistivity behavior indicates that the martensitic transformation from B2 to B19\(^0\) phase starts at 218 K and the other transformation temperatures agree with the previous results. The martensitic reaction exhibits a hysteresis of about 23 K in this alloy.

Positron lifetime \(\tau_m\) increases continuously from 120 to 150 ps with lowering temperature from 380 to 220 K, and then \(\tau_m\) begins to decrease slightly as the temperature...
lowered further (Fig. 1). The $\tau_m$ curve on heating almost follows that on cooling and the hysteresis of $\tau_m$ is very small, although it is about 23 K evaluated from the electrical resistivity change. It is obvious that the majority of positrons are not trapped in any lattice defects since $\tau_m$ of 120 ps at 380 K of the B2 phase agrees with the theoretically calculated value of 118.1 ps as described below. The value of $\chi^2/q$ is very close to unity at any temperature, as shown in Fig. 1, which suggests that there is almost only one kind of positron annihilation site in the specimen at each temperature.

Normally the positron lifetime, which is inversely proportional to electron density (Eq. (1)), decreases slightly with lowering temperature, since electron density in metals increases slightly with decreasing temperature due to the thermal contraction. However, $\tau_m$ of Ni$_{51}$Ti$_{49}$ alloy shows anomalous increase with lowering temperature prior to the martensitic transformation. The simple estimation based on the Eq. (1) indicates about 20% decrease in $n_e$. This anomalous temperature dependence of $\tau_m$ is considered to result from the pre-martensitic behavior of NiTi alloy.

Figs. 2 and 3 show temperature dependence of $\tau_m$ and electrical resistivity in Ni$_{40}$Ti$_{50}$Cu$_{10}$ and Ni$_{35}$Ti$_{55}$Cu$_{15}$ alloys, respectively, which transform from a B2 phase to a B19' phase via a B19 intermediate phase. The electrical resistivity changes of the alloys show good agreement with a previous paper [18]. The transformation temperatures determined by the resistivity measurements are indicated in Figs. 2 and 3 by arrows [18] ($M_s$ and $M'_s$ are transformation start temperatures of B19' and B19, respectively). The $M_s$ temperature of NiTiCu alloys decreases with increasing Cu content while $M'_s$ temperature is approximately constant.

Positron lifetime $\tau_m$ of the Ni$_{40}$Ti$_{50}$Cu$_{10}$ alloy shows monotonous increase from 125 to 132 ps with lowering temperature from 400 K to the $M'_s$ temperature of 342 K (Fig. 2). $\tau_m$ further increases to 141 ps as the temperature is lowered from the $M'_s$ temperature to 190 K. Almost the same change in positron lifetime has been observed on the subsequent heating run with little hysteresis. The positron lifetime of the Ni$_{35}$Ti$_{55}$Cu$_{15}$ alloy shows similar behavior to the Ni$_{40}$Ti$_{50}$Cu$_{10}$ alloy. As temperature is lowered from 400 K to $M_s$ temperature of 235 K, $\tau_m$ continuously increases from 126 to 138 ps. A decrease of $\tau_m$ is observed below 160 K. It is considered again that the majority of positrons annihilate at one kind of annihilation site since $\chi^2/q$ values are almost unity as shown in Figs. 2 and 3.
Fig. 4 shows the change of $t_m$ and electrical resistivity of Ni$_{30}$Ti$_{50}$Cu$_{20}$ alloy. The electrical-resistivity change indicates that the alloy exhibits only one-stage martensitic transformation. This result agrees with the past investigation [18], which showed that NiTiCu alloys do not transform from the B19 to B19$^\circ$ phase if the Cu content is higher than 20 at.%. The electrical-resistivity change shows the martensitic transformation from B2 to B19 phase at 339 K with very little hysteresis of about 2 K. Positron lifetime $t_m$ of the Ni$_{30}$Ti$_{50}$Cu$_{20}$ alloy decreases slightly from 128 to 125 ps as temperature is lowered in the temperature range of B2 phase. $t_m$ increases from 125 to 155 ps with the martensitic transformation. Anomalous pre-martensitic increase of $t_m$ is not observed in the B2 phase of this alloy in contrast to Ni$_{51}$Ti$_{49}$, Ni$_{40}$Ti$_{50}$Cu$_{10}$ and Ni$_{35}$Ti$_{50}$Cu$_{15}$ alloys. The value of $t_m$ about 155 ps obtained in the B19 phase is much longer than the theoretically calculated value of 115.6 ps.

Anomalous temperature dependence of $t_m$, is observed not only in Ni$_{51}$Ti$_{49}$ alloy, but also in Ni$_{40}$Ti$_{50}$Cu$_{10}$ and Ni$_{35}$Ti$_{50}$Cu$_{15}$ alloys with lowering temperature prior to the martensitic transformation. On the other hand, $t_m$ in a B2 phase of Ni$_{30}$Ti$_{50}$Cu$_{20}$ alloy shows normal behavior. These behaviors of $t_m$ are correlated with the intrinsic electronic-structure change in NiTi alloys.

The positron lifetimes of B2, B19 and B19$^\circ$ structures of the NiTi alloy are obtained to be 118.1, 115.6, and 122.8 ps, respectively, by first-principle calculation. The calculated positron lifetime of B2 structure shows good agreement with the experimental values of NiTi and NiTiCu alloys at about 380–400 K as shown in Figs. 1–4. It is obvious that non-stoichiometry in binary Ni$_{51}$Ti$_{49}$ alloy is compensated with anti-site atoms and that the majority of positrons are not trapped in any vacancy-type lattice defects. However, experimental positron lifetime of B19$^\circ$ phase is about 30 ps longer than calculated one and experimental B2 value gradually comes up as the temperature is lowered. Experimental $t_m$ for B19 phase in Ni$_{30}$Ti$_{50}$Cu$_{20}$ alloy is almost 40 ps longer than calculated value. These big differences between the experimental results and calculated ones can not be explained by existing theories.

It is considered that the temperature change of $t_m$ in NiTi alloys is associated with the pre-martensitic phenomena of the alloys. It is reported, for example, that the NiTi alloys have different soft-phonon mode according to the martensitic transformation paths. Elastic constants of $c' = (c_{11} - c_{12})/2$ and $c_{44}$ of all the NiTi and NiTiCu alloys soften with lowering temperature but Cu-addition increases $c_{44}$ which controls the transformation of B19$^\circ$ [19]. Phonon dispersion curves of TA2 phonon branch for NiTi and NiTiCu alloys indicate that the former has two dips near the position of $q = 1/3$ and 1/2 and the latter has only one dip near $q = 1/2$ [20,21]. These differences of soft-phonon mode may have influences on the temperature change of positron lifetime. Further investigation into details is required.

5. Summary

The positron lifetime and electrical resistivity measurements of NiTi and NiTiCu alloys were carried out at temperatures between 100 and 400 K. Anomalous positron lifetime changes were found in Ni$_{51}$Ti$_{49}$, Ni$_{40}$Ti$_{50}$Cu$_{10}$ and Ni$_{35}$Ti$_{50}$Cu$_{15}$ alloys which exhibit B2–B19$^\circ$ and B2–B19–B19$^\circ$ phase transformations, respectively. Positron lifetime increases anomalously with decreasing temperature at temperatures higher than the transformation temperature into a B19$^\circ$ phase. On the other hand, positron lifetime does not show any anomaly in the B2 phase of Ni$_{30}$Ti$_{50}$Cu$_{20}$ alloy which shows only a B2–B19 phase transformation. It is considered that the temperature change of $t_m$ in NiTi alloy is correlated with the pre-martensitic phenomena of the alloy.

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