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Two-stage transformation of aluminum-containing NiTi

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Abstract

Measurements of electrical resistivity, ultrasonic velocity and attenuation for equiatomic NiTi and $Ni_{50}Ti_{49}Al_1$ were performed in order to characterize the thermoelastic martensitic transformation during cooling. The NiTi shows a one-stage transformation, essentially, because a premartensitic phenomenon is negligibly faint. The ultrasonic anomalies in NiTi appear near the temperature at a faint resistivity-peak, which correspond to lattice softening at the start temperature of martensitic transformation from the high-temperature phase to the low-temperature phase. The resistivity of $Ni_{50}Ti_{49}Al_1$ has a negative temperature coefficient over the wide temperature range from room temperature to154 K, and indicates a large peak. Such an anomaly in resistivity corresponds to an enhanced premartensitic phenomenon, where ultrasonic anomalies caused by a two-stage transformation are observed which accompany a large change in electrical resistivity. However, a resistivity peak in the aluminum-containing NiTi is formed at lower temperature than those at ultrasonic anomalies by over 40 K, and the temperature at the resistivity peak is not one characterizing the transformation behavior. It proved helpful to measure the ultrasonic properties in comparison with the electrical resistivity in order to characterize successive transformations in the temperature range of a premartensitic phenomenon of NiTi enhanced by addition of aluminum.

Keywords: NiTi alloy; NiTi(Al) alloy; Martensitic transformation; Electrical resistivity; Ultrasonic velocity; Ultrasonic attenuation

1. Introduction

It is known that a thermoelastic martensitic transformation in the near-equiatomic NiTi alloy leads to the useful mechanical properties of a shape memory and pseudoelasticity [1,2]. Investigations on its transformation have often been performed by measurements of mechanical and physical properties [3–13]. For a better understanding of the transformation behavior, it proved necessary to measure various features of NiTi because the transformation is complicated, depending on the composition and the thermal history such as the repetition of the transformation by thermal cycling and the thermal treatment [14–16]. Additional elements such as iron [17–19] and aluminum [20–24] influence not only the transformation temperature but also the path of the transformation, and bring about a premartensitic phenomenon. The premartensitic phenomenon was also shown in binary NiTi alloy by the measurement of electron diffraction, corresponding to the appearance of the intermediate (rhombohedral) phase when the high-temperature phase

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(CsCl) of NiTi is martensitically transformed into the low-temperature (monoclinic) phase [25–28]. Because the electrical resistivity is sensitive to the phase change in NiTi, this transformation behavior can be detected as follows: the resistivity increases as the intermediate phase is formed, and begins to decrease on the transformation to the low-temperature phase, resulting in a maximum, that is, a peak in the electrical resistivity. Frequently, alloying with additional elements leads to an alteration of transformation process in NiTi. Recently, the transformation of NiTi containing iron is verified by detailed experiments of the electron diffraction and transmission electron microscopy during cooling and its transformation process is also characterized by measuring electrical and ultrasonic properties [17]. A study on the transformation pathway is necessary for making application to a mechanical actuator, and important in understanding the transformation mechanism and the stability of each phase.

So far, the transformation behavior of NiTi influenced by addition of aluminum has been scarcely characterized by measurements of physical properties and precise determination of crystal structure. As effects of aluminum addition for the transformation of NiTi are taken to be important in characterizing transformation behavior in the temperature range of an enhanced premartensitic phenomenon, the transformation behavior for $Ni_{50}Ti_{50-x}Al_x$ was revealed by measurements of electrical and ultrasonic properties. In such a premartensitic temperature region, the electrical resistivity increases with decreasing the temperature and an ultrasonic anomaly appears which suggest a new phase change [21]. However, an ultrasonic measurement has not yet been performed for the NiTi containing aluminum contents lower than 1.5 at%. Therefore, for a better understanding of the transformation behavior of NiTi alloyed with additive elements, it is necessary to characterize the transformation behavior by using an ultrasonic technique, because the ultrasonic measurement is effective for the identification of the transformation with a lattice softening such as the thermoelastic martensitic transformation. In the present study, the electrical resistivity and ultrasonic properties were measured on the transformation for NiTi containing lower aluminum content and were compared with the equiatomic NiTi alloy, in order to reveal substitutional effect of aluminum for titanium on the transformation pathway during cooling.

2. Experimental procedure

The alloy ingots of NiTi and nickel-enriched NiTi were prepared from nickel (purity, 99.99%) and titanium (purity, 99.9%) by electron-beam melting in a vacuum of 10^{-2} Pa [29]. Aluminum (purity, 99.999%) was added to the nickel-enriched NiTi ingot by the same melting method. After several remelts, the alloy ingots were annealed at 1273 K in a vacuum of 10^{-4} Pa for homogenization, and the specimens for the measurements were cut out of the ingots. After reannealing under the above-mentioned annealing condition and furnace-cooling, measurements of electrical resistivity, ultrasonic velocity and ultrasonic attenuation were performed during first cooling in the temperature range from room temperature to about 90 K. The resistivity was precisely measured by a four-probe potentiometric method. The ultrasonic properties for the longitudinal wave was measured using a transducer of X-cut quartz operated at a frequency of 10 MHz. The measurement of ultrasonic velocity was performed by a pulse-echo overlap method and the attenuation was determined from intensities of the first and the second pulse-echo. The relative accuracy for measuring the resistivity, the ultrasonic velocity and the attenuation was estimated within 0.001%, 0.01% and 0.5%, respectively [30]. The alloys prepared in the present study were equiatomic NiTi and $Ni_{50}Ti_{49}Al_1$.

3. Experimental results and discussion

3.1. Electrical resistivity

The electrical resisitivity versus temperature curves during cooling for equiatomic NiTi and $Ni_{50}Ti_{49}Al_1$ are shown in Fig. 1, together with that for $Ni_{50}Ti_{48.5}Al_{1.5}$ [21]. A faint premartensitic

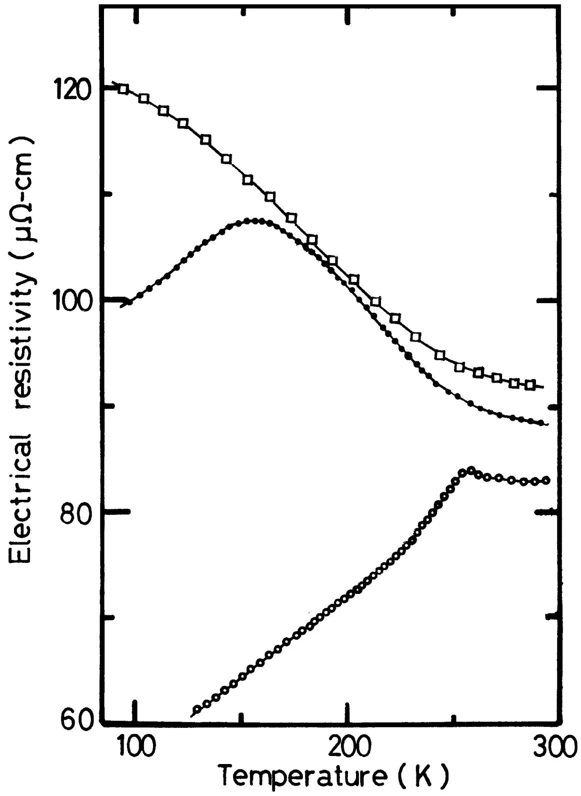

Fig. 1. Electrical resistivity versus temperature curve for NiTi and $Ni_{50}Ti_{49}Al_1$, together with that of $Ni_{50}Ti_{48.5}Al_{1.5}$ [21]. Open and closed circles and square show NiTi, $Ni_{50}Ti_{49}Al_1$ and $Ni_{50}Ti_{48.5}Al_{1.5}$, respectively. The increase in resistivity corresponds to the premartensitic phenomenon, which is markedly enhanced by addition of aluminum.

phenomenon appears in the equiatomic NiTi, because a peak in the resistivity appears at 258 K which is attributable to the start of transformation to the low-temperature phase after the intermediate phase is formed during cooling. However, the formation of the intermediate phase is negligible because the peak is so faint. Such resistivity behavior is the same as that of previous results [8,9] though the transformation temperature varies. The electrical resistivity in $Ni_{50}Ti_{48.5}Al_{1.5}$ [21] has a negative temperature coefficient in the temperature range of measurement, which implies that the premartensitic phenomenon is so enhanced by the addition of aluminum. It is suggested on the previous investigation of Ni_{50}-$Ti_{48.5}Al_{1.5}$ that the transient regime from the high-temperature phase to the intermediate phase is expanded, drastically [21]. On the other hand, an intensified premartensitic phenomenon is also observed in the $Ni_{50}Ti_{49}Al_1$ alloy because of the appearance of a large peak in resistivity at 154 K, as shown in Fig. 1. The transformation of Ni_{50}-$Ti_{49}Al_1$ is considered as a medium behavior in comparison with transformations of NiTi and $Ni_{50}Ti_{49}Al_{1.5}$ alloys. Therefore, with increasing the content of aluminum the resistivity increases and the transient region is remarkably broadened where the high-temperature phase is martensitically transformed. It is identified on the basis of the structural and the compositional analysis, using a X-ray diffractometer and an electron probe micro-analyzer that the present alloys show the high-temperature phase of NiTi with the CsCl structure at room temperature and the aluminum-containing NiTi form a solid solution with aluminum though a small amount of the Ti_2Ni (FCC) precipitates from the NiTi phase [31]. Therefore, the alteration in the transformation behavior of NiTi phase, as shown in Fig. 1, is attributable to the influence of aluminum solid-soluted in NiTi phase, which depends strongly on the aluminum content as well as the addition of iron and enriched nickel [8]. It was reported in $Ni_{50}Ti_{48.5}Al_{1.5}$ [21] that a broad dip in ultrasonic velocity appears at 180 K which is associated with a drastic change in electrical resistivity and the ultrasonic attenuation shows a peak. These ultrasonic anomalies imply the presence of a transition. It is suggested that this new transformation correspond to the appearance of an incommensulate phase in the premartensitic region where the high-temperature phase is martensitically transformed into the intermediate phase. Measurements such as the electron diffraction and the transmission electron micro-image have been scarcely carried out in order to reveal the structural feature, and the presence of the intermediate phase has not yet been clear on NiTi containing aluminum though it is predicted from the detection of a peak in resistivity. As the crystal lattice becomes unstable upon transformation, a clearer characterization of the transformation behavior on NiTi and $Ni_{50}Ti_{49}Al_1$ is acquired by the ultrasonic measurement as described below.

3.2. Ultrasonic velocity

The ultrasonic velocity versus temperature curves for the NiTi and $Ni_{50}Ti_{49}Al_1$ alloys are shown in Fig. 2, in which a dip is observed for each alloy. A dip in the ultrasonic velocity of NiTi is detected at 254 K, which corresponds to the lattice instability, that is, a softening of crystal structure incidental to the process of shearing during martensitic transformation to the low-temperature phase because the electrical resistivity decreases remarkably, as shown in Fig. 1. The dip in velocity appears near the temperature of a small peak in resistivity, where the high-temperature phase begins to transform martensitically to the low-temperature phase because the trace of transformation to the intermediate phase is negligibly small in the behavior of resistivity. It is taken to be reasonable that the reduction in elastic modulus caused by the lattice instability, namely, the dip in ultrasonic velocity is formed in the vicinity of the martensitic start temperature (M_s). The temperature and the velocity at a dip vary with the addition of aluminum remarkably. The minimum value in velocity for $Ni_{50}Ti_{49}Al_1$ is much smaller than that for the NiTi in spite of the larger velocity on high-temperature phase. This implies that aluminum-containing enhances the lattice instability due to the transformation. Moreover, although the ultrasonic velocity for $Ni_{50}Ti_{49}Al_1$ reaches a minimum value at 206 K, the behavior of velocity has a tendency to show two dips because the shoulder in the dip is detected at 220 K, as shown in Fig. 2. Therefore, the velocity versus temperature curve for $Ni_{50}Ti_{49}Al_1$ suggests the appearance of two transformations during cooling. The pathway of the transformation in NiTi phase markedly depends on the aluminum content within the range up to 1.5 at%.

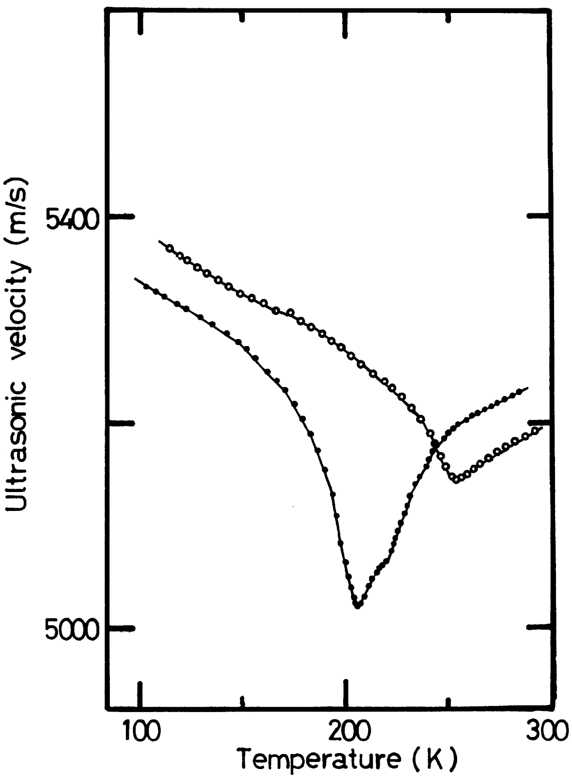

Fig. 2. Ultrasonic velocity versus temperature curve for NiTi and $Ni_{50}Ti_{49}Al_1$. Open and closed circles show NiTi and $Ni_{50}Ti_{49}Al_1$, respectively. Each alloy has an anomalous dip in the velocity.

3.3. Ultrasonic attenuation

The ultrasonic attenuation versus temperature curves for the NiTi and $Ni_{50}Ti_{49}Al_1$ are shown in Fig. 3. The attenuation for the NiTi shows a sharp peak at 253 K and a hump in the vicinity of 200 K, and the attenuation of the high-temperature phase is smaller than that of the low-temperature phase, as shown in Fig. 3. The sharp peak in the attenuation is attributable to the lattice instability in the high-temperature phase which start to transform to the low-temperature phase because the electrical resistivity begin to decrease, drastically, as shown in Fig. 1, though the additional instability may overlap which is associated with the transformation to the intermediate phase. On the other hand, the hump in attenuation is pronounced in the temperature range where the NiTi transform to the martensite structure of the low-temperature phase, substantially, because the hump is formed in the vicinity of the finish temperature of martensitic transformation (M_f) which is estimated to be about 200 K from the temperature dependence of the resistivity for NiTi. It is thought that the generation of the hump in the attenuation is caused by the development of a

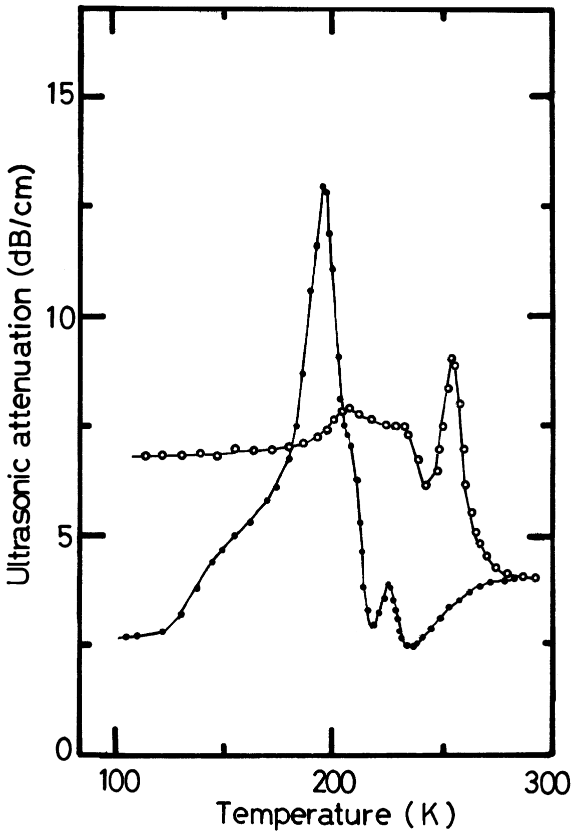

Fig. 3. Ultrasonic attenuation versus temperature curve for NiTi and $Ni_{50}Ti_{49}Al_1$. Open and closed circles show NiTi and $Ni_{50}Ti_{49}Al_1$, respectively. Anomalous peaks are seen in the attenuation.

martensite and microstructure during the transformation which depend on the process of self-adjustment of local region under the inner stress influenced by the volume change and the microstructure with the progress of transformation. Therefore, in measuring the ultrasonic properties such as the velocity and the attenuation, the phase transition on equiatomic NiTi is detected such as a one-stage transformation, though the premartensitic phenomenon is observed, faintly, in the resistivity versus temperature curve. This implies that the measurement of the resistivity is available in the detection and characterization of the faint premartensitic phenomenon. However, the measurement of the ultrasonic attenuation is important in observing the pathway of transformation of which the temperature range is considerably broadened with an enhanced premartensitic phenomenon due to aluminum addition as described below.

The ultrasonic attenuation for $Ni_{50}Ti_{49}Al_1$ shows two peaks at 225 and 196 K, as shown in Fig. 3, which are attributable to a two-stage transformation, that is, a high-temperature phase → intermediate phase → low-temperature phase. The attenuation peak on the transformation to the low-temperature phase is much larger than that for the NiTi in the temperature range of transformation. Therefore, the pathway of the transformation for $Ni_{50}Ti_{49}Al_1$ shows the behavior of two-stage transformation accompanied by a more softening of lattice. However, as the transformation behavior may be more complex because of the shape of attenuation peak, it is necessary to observe the structural feature by measuring the electron diffraction and the transmission electron micro-image.

3.4. Temperature coefficient of resistivity and ultrasonic anomalies

The temperatures at a small peak in the resistivity, a dip in the velocity and a sharp peak in the attenuation for the NiTi are close to one another, and it is apparent that the transformation to the low-temperature phase brings about the anomalous behavior in the resistivity and the ultrasonic properties. However, not only the change of the transformation pathway from a one-stage to a two-stage but also a considerable difference between the temperature at a resistivity peak and ultrasonic anomalies are observed in the transformation of $Ni_{50}Ti_{49}Al_1$. For a more precise characterization of the anomalous features in the transformation behavior of $Ni_{50}Ti_{49}Al_1$, the temperatures at the attenuation peak (a_p), the velocity minimum (v_m) and the shoulder in velocity (v_s) are shown in Fig. 4, together with the temperature coefficient of the electrical resistivity which is calculated from the resistivity–temperature curve in Fig. 1. The temperature coefficient versus temperature curve for $Ni_{50}Ti_{49}Al_1$ alloy shows a minimum of about $-270\,n\Omega\,cm\,K^{-1}$ at 218 K and an arrest of $-220\,n\Omega\,cm K^{-1}$ near 200 K. The

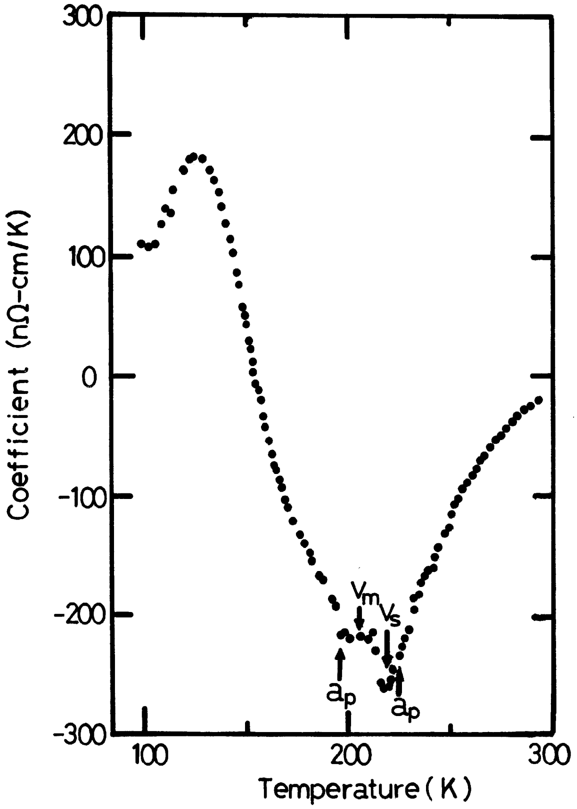

Fig. 4. Temperature coefficient of electrical resistivity as a function of temperature for $Ni_{50}Ti_{49}Al_1$, which is calculated from the experimental result shown in Fig. 1. The a_p, v_m and v_s indicate the temperatures at the sharp peak in the attenuation, and minimum and shoulder in the velocity, respectively, which are obtained in Figs. 2 and 3.

characteristic temperatures of a_p, v_m and v_s are positioned in the temperature region where the electrical resistivity drastically increases with decreasing temperatures, as shown in Fig. 4. Therefore, the two attenuation peaks and the dip and the shoulder in the velocity are accompanied with a drastic change in the resistivity. Moreover, it is assumed in the transformation of $Ni_{50}Ti_{49}Al_1$ that the resistivity peak detected at 154 K does not characterize the transformation behavior because the resistivity peak and ultrasonic properties are about 40 K or more apart in temperature, as distinct from the change in the properties during the transformation of equiatomic NiTi. Therefore, the ultrasonic measurement is effective for indicating the transformation behavior that is associated with a premartensitic phenomenon of NiTi enhanced by additional elements.

4. Conclusion

Characterization of the transformation behavior was performed by measuring the electrical resistivity, the ultrasonic velocity and the attenuation during cooling for equiatomic NiTi and $Ni_{50}Ti_{49}Al_1$. Anomalies for the NiTi are detected which are a small peak in the resistivity, a dip in the velocity and a sharp peak in the attenuation. These anomalies correspond to the transformation of the high-temperature phase to the low-temperature phase, and appear in the vicinity of the start temperature of the transformation. Moreover, a hump in attenuation is formed near the finish temperature of the transformation, which is connected with a microstructure and the inner stress due to the volume change during the transformation. The $Ni_{50}Ti_{49}Al_1$ has an enhanced premartensitic phenomenon because of showing a broad and large peak in the resistivity, where anomalies in ultrasonic properties corresponding to a two-stage transformation appear in the temperature region showing the most drastic change in the resistivity. In contrast to the NiTi, the temperature at the resistivity peak does not characterize the behavior of martensitic transformation with the lattice softening for $Ni_{50}Ti_{49}Al_1$. The ultrasonic measurement is helpful in detecting the behavior of successive transformation in the temperature range of a premartensitic phenomenon enhanced by addition of aluminum to NiTi.

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