Thermal and transport properties of as-grown Ni-rich TiNi shape memory alloys

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Electrical resistivity, Seebeck coefficient, specific heat and thermal conductivity measurements on the Ti50, xNi50, x (x = 0.0–1.6 at%) shape memory alloys are performed to investigate their thermal and transport properties. In this study, anomalous features are observed in both cooling and heating cycles in all measured physical properties of the slightly Ni-rich TiNi alloys (x < 1.0), correspond to the transformation between the B19' martensite and B2 austenite phases. Besides, the transition temperature is found to decrease gradually with increasing Ni content, and the driving force for the transition is also found to diminish slowly with the addition of excess Ni, as revealed by specific heat measurements. While the signature of martensitic transformation vanishes for the Ni-rich TiNi alloys with x > 1.3, the characteristics of strain glass transition start to appear. The Seebeck coefficients of these TiNi alloys were found to be positive, suggesting the hole-type carriers dominate the thermoelectric transport. From the high-temperature Seebeck coefficients, the estimated value of Fermi energy ranges from ~1.5 eV (Ti48.4Ni51.6) to ~2.1 eV (Ti50Ni50), indicating the metallic nature of these alloys. In addition, the thermal conductivity of the slightly Ni-rich TiNi alloys with x < 1.0 shows a distinct anomalous feature at the B19' → B2 transition, likely due to the variation in lattice thermal conductivity.

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1. Introduction

The titanium–nickel are well established as shape memory alloy due to its excellent performance, i.e. good shape memory effect and superelastic behavior, which originates from a spontaneous lattice-distorting transition called as martensitic transition. Among many shape memory alloys, TiNi-based alloys are the most important practical materials due to their superior shape memory and mechanical properties [1,2]. Moreover, the equiatomic TiNi alloy goes through a first order phase transition from the cubic austenite phase (B2) to a monoclinic martensite phase (B19') upon cooling process. Recent theoretical studies showed that the phase transition between austenite and martensite phases occurs due to the relaxation of the monoclinic angle, ascribed to the evolving of the Fermi-surface nested regions [3]. It is found that the atomic shifts and the changes in lattice parameters of TiNi near phase transition are considerably large, hence the transition takes place in two steps: cubic-orthorhombic-monoclinic [4]. Besides, the pre-martensitic phase transition appears as a result of the coupling of phonons with the Fermi-surface nested electronic states, which is the source of origin for the phonon anomaly and soft phonons in TiNi [5]. In fact, the B19' phase of TiNi is unstable relative to a base-centre orthorhombic structure that cannot store shape memory at the atomic level [6], however the B19' structure is stabilized by an applied or residual internal stresses. Moreover, it is known that the martensitic transition in TiNi is extremely sensitive to doping or thermo-mechanical treatment. In particular, TiNi alloy is often doped with a third element such as Cu or Fe [7–9], and also doped with excess Ni [10–14], to further modify its shape memory and mechanical properties.

Pure TiNi (Ti50Ni50) undergoes a B2 → B19' martensitic transition near room-temperature [8]. For the Ni-rich TiNi (Ti50, xNi50, x) alloys, the existence of martensitic transition remains intact until x < 1.3. However, the martensitic transition temperature (M_s) and the latent heat associated with the transition show a drastic reduction with increasing Ni content [14]. Besides, excess Ni causes the defect-induced precursor state with pre-martensitic phase which appears above M_s [15], and such a nanostructure phase is not
expected for the parent B2 phase [16]. The appearance of the defect-induced precursor state (nanocluster or tweed pattern) is quite common in many shape memory alloys such as Ti–Ni–Fe [15,17,18], Ni–Al [19], and Co–Ni–Ga [20]. For high excess Ni alloys with $x \geq 1.3$, the electrical resistivity and dynamic mechanical studies showed that the martensitic transition is absent [14]. However, it is noticed that the high Ni-rich TiNi alloys actually undergo a new type of transition called strain glass transition at $T_0$ [13,14].

Most of reports on the Ni-rich TiNi alloys in the literature are in the metallurgical point of view and only very few studies focused on the thermoelectric properties such as Seebeck coefficient and thermal conductivity. It is well-known that the Seebeck coefficient is a sensitive probe of the electronic instability around the Fermi surface, such as the nesting of Fermi surface induced by the martensitic transition, and the thermal conductivity measurement could provide valuable information about the interplay between the lattice and charge degrees of freedom in the TiNi-based alloys [8,9]. In the present work, we thus performed an extensive investigation on thermal and transport properties of the Ni-rich TiNi alloys, namely Ti$_{50-x}$Ni$_{50+x}$ ($x = 0.0–1.6$ at.%)$. The values of transition temperature are estimated using highly sensitive probes such as Seebeck coefficient and thermal conductivity, and effort has also been made to realize the physical significance and possible origin for the anomalous features near the martensitic transition in these Ni-rich alloys.

2. Experiments

Ti$_{50-x}$Ni$_{50+x}$ ($x = 0.0–1.6$ at.%) shape memory alloys were prepared using a vacuum arc remelter (VAR). The titanium and nickel elements with total mixture of about 120 g were re-melted six times in an argon atmosphere, and the obtained melts were passed through a gas purifier to reduce its oxygen content. The weight loss during the re-melting process is less than 0.01%. Finally, the purified samples were homogenized at 900 °C for 1 h and then cooled down to room temperature by water quenching. The chemical compositions of Ti$_{50-x}$Ni$_{50+x}$ ($x = 0–1.6$ at.%) samples have been checked by Electron Probe Microanalyzer (EPMA, JAX-8200SX, JEOL Ltd., Tokyo, Japan), in which eight spots for each sample were examined for the estimation of composition. The estimated average composition of the Ni doped TiNi-based alloys (with eliminating the extreme values on either sides) are about Ti$_{48.98}$Ni$_{51.02}$ ± 0.14 at.%, Ti$_{48.98}$Ni$_{51.02}$ ± 0.24 at.%, Ti$_{48.98}$Ni$_{51.03}$ ± 0.08 at.%, and Ti$_{48.40}$Ni$_{51.60}$ ± 0.29 at.% for the Ti$_{49.98}$Ni$_{50.04}$, Ti$_{49.98}$Ni$_{50.07}$, Ti$_{49.98}$Ni$_{50.1}$, and Ti$_{48.40}$Ni$_{51.6}$ samples respectively. Temperature-dependent electrical resistivity measurements on the Ni-rich TiNi alloys were carried out using a standard four-probe technique. Seebeck coefficient and thermal conductivity of these TiNi-based samples were simultaneously measured using a direct heat pulse technique in a closed cycle refrigerator over the temperature range of 10–400 K. More details about these characterization techniques can be found elsewhere [21]. Specific heat measurements were also performed on these samples by ac calorimeter in the temperature range from 100 K to 350 K, using chopped light as a heat source.

3. Results and discussion

3.1. Electrical resistivity

Measured electrical resistivity data, $\rho(T)$ of the Ti$_{50-x}$Ni$_{50+x}$ (0.0 ≤ $x$ ≤ 1.6 at.%) shape memory alloys during cooling and heating cycles are displayed in Figs. 1 and 2. Room-temperature resistivity of these TiNi-based alloys is found to increase gradually with increase in Ni concentration from ~89 $\mu$Ω cm for Ti$_{50}$Ni$_{50}$ to ~118 $\mu$Ω cm for Ti$_{48.7}$Ni$_{51.3}$, and then decreased to ~95 $\mu$Ω cm (Ti$_{48.4}$Ni$_{51.6}$). Similarly, the estimated value of residual resistivity also increases slowly from ~38 $\mu$Ω cm for Ti$_{50}$Ni$_{50}$ to ~158 $\mu$Ω cm for Ti$_{48.4}$Ni$_{51.6}$.

![Fig. 1. Temperature-dependent electrical resistivity, $\rho(T)$ of the (a) Ti$_{50}$Ni$_{50}$, (b) Ti$_{48.7}$Ni$_{51.3}$ and (c) Ti$_{48.4}$Ni$_{51.6}$ alloys during cooling and heating cycles.](image-url)

![Fig. 2. (a) Temperature dependence of electrical resistivity, $\rho(T)$ of the Ti$_{49}$Ni$_{51}$ in the cooling and heating cycles, and the $\rho(T)$ curves of (b) Ti$_{48.7}$Ni$_{51.3}$ and (c) Ti$_{48.4}$Ni$_{51.6}$ alloys during heating process. Inset of Fig. 2b shows the plot of $d\rho/dT$ versus $T$ (y-axis in left panel). The freezing temperature $T_0$ is determined as temperature at which the second derivative of the resistivity changes its sign.](image-url)
The increasing trend of residual resistivity with respect to Ni content (x) indicates the enhancement in impurity scatterings for the Ni-rich alloys. However, the residual resistivity of the Ti50Ni50 alloy is still lower than that of the reported value [22], suggesting the highly ordered nature of the present sample.

Upon cooling, the resistivity of equiatomic Ti50Ni50 shows a sharp rise followed by a sudden fall in the form of well-defined peak at around 295 K, as shown in Fig. 1a. For further decrease in temperature, the resistivity of the Ti50Ni50 alloy decreases gradually which represents a typical metallic behavior. The distinct anomaly at 295 K in the ρ(T) curve of Ti50Ni50 corresponds to B2 → B19′ transition [8,9,23], due to the relaxation of monoclinic angle, ascribed to the Fermi surface nested regions [3]. On the other hand, the heating curve of ρ(T) for Ti50Ni50 shows a weaker anomaly (B19′ → B2) which occurs at higher temperature of about 334 K [8,24].

The starting/peak/finishing temperature of the martensite and austenite phases has been represented by \( T_m/T_A/T_f \) and \( A_r/A_p/A_t \) respectively, as shown in Fig. 1. However, the exact value of \( A_p \) is not easy to identify because the resistivity changes are not obvious at the transition temperature. It is due to the fact that the transition temperatures \( (A_p/A_t) \) of the B19′ → B2 transformation in the resistivity scans of TiNi-based alloys were found to be shifted to higher temperatures than that of the actual values due to a significant thermal hysteresis during martensitic transformations [25]. The characteristics of the \( ρ(T) \) curves are found to be strongly dependent on the Ni content, as clearly seen in Figs. 1 and 2. For the low Ni-rich TiNi alloys with x ≤ 1.0% (Figs. 1b, c and 2a), the \( ρ(T) \) curves show similar behaviors to that of the parent Ti50Ni50 i.e. a well-defined peak corresponds to \( M_B \) a weaker anomalous feature at \( A_p \) and overall show metallic behavior. For the high Ni-rich TiNi alloys with x > 1.3%, it is found that the \( ρ(T) \) characteristics tend to show a semiconducting-like behavior with a negative temperature coefficient (see Fig. 2b and c), and the signature of martensitic transformation seems to be vanished. The negative temperature coefficient in \( ρ(T) \) curve is a characteristic of the strain glass transition that occurs in the Ni-rich TiNi alloys with x > 1.3%, due to the local stress induced by the excess Ni (point-defects) in the TiNi lattice [14]. It is noticed that the resistivity data of these alloys show an inflection point at the freezing temperature (see inset of Fig. 2b), known as the strain glass transition temperature \( T_G \), as marked by arrows in Fig. 2b and c. At \( T_G \), the high-temperature unfrozen strain glass state transforms into a frozen strain glass state, which exhibits unusual frequency-dependence behaviors in the dynamic mechanical properties [14]. Above the strain glass transition, these strain glass alloys stay in their unfrozen state [24].

In order to interpret the significance of these three phases (martensite, austenite and strain glass) in the TiNi-based alloys, the values of MP, AP and TG are plotted against Ni content in Fig. 3. All alloys are in the parent phase (B2) at high temperatures, and however the phase transition follows diverse paths and results in a very different phase with increase in Ni concentration (x). The values of MP and AP are found to decrease noticeably with increasing Ni content. The estimated thermal hysteresis, determined from the difference between the values of AP and MP of these TiNi-based alloys is also plotted against Ni content (inset in Fig. 3). It is noticed that the magnitude of thermal hysteresis for Ni-rich TiNi alloys with x ≤ 1.0 is smaller than that of the parent compound TiNi. However, the TiNi alloys with x ≤ 1.0 transform directly from the B2 (B19′) phase into B19′ (B2) at their MP (AP) during the cooling (heating) process. For Ni-rich TiNi alloys with x ≥ 1.3, high-temperature unfrozen strain glass state transforms into a frozen strain glass state at their freezing temperature \( T_G \) [13,14], instead of transforming into the martensite phase upon cooling. In Sec. 3.2, the martensitic transition will be further explored using the highly sensitive Seebeck coefficient measurement, which can help us to evaluate the values of transition temperatures accurately, and also check the presence of a precursor state if any, which was seen in the earlier report on the Ni-rich TiNi alloys [14].

3.2. Seebeck coefficient

The temperature dependence of the Seebeck coefficient, \( S(T) \) of the Ti50$_x$Ni50$_{1-x}$ alloys is shown in Fig. 4. The measured Seebeck coefficient of the all TiNi-based alloys is found to be positive in the entire temperature range investigated, suggesting that the majority charge carriers are holes. The room-temperature S values vary from 17 to 9 \( \mu \)V/K which shows a strong dependence with Ni content. The maximum room-temperature S value of about −17 \( \mu \)V/K is obtained for the Ti50Ni50, and the S value gradually reduces to −9 \( \mu \)V/K with Ni content up to x = 0.7, and then increases slightly to ~10 \( \mu \)V/K for further addition of Ni content. Generally, both electrons and holes contribute to the thermoelectric transport in the electrically conducting samples. In the presently studied Ti50$_x$Ni50$_{1-x}$ alloys, the increase in the number of electrons which has a higher mobility than the holes might lead to the observed reduction in the S value for the Ni-rich TiNi alloys (Fig. 4). The S(T) curve of the Ti50Ni50 alloy shows a sharp rise at about ~310 K and ~317 K in the cooling and heating cycles respectively, with an thermal hysteresis of about 7 K (Fig. 4a). For the low Ni excess TiNi alloys with x ≤ 1.0, all of the S(T) curves show a clear anomalous feature due to the one-stage transformation of B2 ↔ B19′ (Fig. 4b, c and d). For higher Ni content (x ≥ 1.3), the martensitic transition is found to be absent in the S(T) characteristics (Fig. 4e and f), consistent with the resistivity data (Fig. 2b and c). It is important to mention here that there is no sign of the intermediate phase [4,8] or pre-martensitic phase [14] in the parent and Ni-rich TiNi alloys, as evident from the highly sensitive S(T) data presented here. The sharp variation in the S(T) near the martensitic transition indicates a considerable modification in the density of states near the Fermi surface. It is also well-known that the peaks in the DOS near \( E_F \) may cause lattice instabilities which possibly lead to the observed structural transitions [4,5,23].
Below the martensitic transition, the \( S(T) \) characteristics of the parent and Ni-rich TiNi alloys follow a typical metallic diffusive behavior, and a hump below 50 K is clearly visible which marked by the arrows in Fig. 4. This low-temperature feature in these alloys is most likely due to the phonon drag effect, which is found to be suppressed in the earlier report on the Ti50Ni50 alloy due to the disorder [22]. It is also noticed that the \( S(T) \) curves of these alloys are quite linear at high temperatures above the phase transition. For ordinary metals, the Seebeck coefficient is expected to be linear with temperature according to Mott’s formula, \( S = \frac{e^2}{2\pi^2k_B^2T} \). Assuming a one-band model with an energy-independent relaxation time, \( E_F \) is the Fermi energy and \( k_B \) is the Boltzmann constant. By fitting the \( S(T) \) data in the austenitic B2 phase, we obtained the value of Fermi energy \( (E_F) \) for these TiNi-based alloys, which are listed in Table 1. The estimated value of Fermi energy decreases gradually with increasing Ni content from \( -2.1 \) eV (Ti50Ni50) to \( -1.5 \) eV (Ti48.4Ni51.6), which is in good agreement with the metallic nature of these TiNi-based alloys. Hence, the addition of excess Ni atoms onto the Ti sites of TiNi alloy has resulted in the change in \( E_F \) and its electronic properties, which in turn has a strong influence on the martensitic transition [7–9,26].

The deduced values of \( M_s \) and \( A_s \) for the Ni-rich TiNi alloys from the Seebeck coefficient data are listed in Table 1, which demonstrates the effect of excess Ni on the martensitic and austenitic transitions in the alloys. It is found that the separation between \( M_s \) and \( A_s \) is quite noticeable with a value of about \(-7\)–\(-10\) K. However, such a value is considerably small compared to the hysteresis temperature determined from the resistivity data (see inset of Fig. 3). Hence, we argue here that Seebeck coefficient measurements are a more reliable probe to determine the values of \( M_s \) and \( A_s \) for the TiNi-based alloys. It is also important to mention that a peak in the DOS near the Fermi level may be the cause of lattice instability in TiNi [23] and the atomic distortions associated with the phase transition are also quite large [4], which could result in a change in the monoclinic angle due to the presence of the nested regions of the Fermi surface in TiNi [3]. These factors may lead to a sharp variation in Seebeck coefficients near the phase transitions, as seen in Fig. 4. Therefore, the observed stable martensite B19’ phase until \( x = 1.0 \) is most likely due to the survival of the peak in the DOS near \( E_F \) upon low Ni doping. However, the contribution of electronic and lattice parameters are equally important to understand the thermoelectric properties of the Ni-rich TiNi alloys, which will be further examined as we discuss the thermal conductivity data of these alloys in Sec. 3.4.

### 3.3. Specific heat

The specific heat curves, \( C_p(T) \) of the \( Ti_{50-x}Ni_{50-x} \) alloys with \( x \leq 1.0 \) are shown in Fig. 5. From the \( C_p(T) \) plots in the cooling and heating cycles, the substantial variations across the martensitic phase transition with a noticeable thermal hysteresis are observed which indicate the presence of a strong first-order transition in the NiTi alloys. However, the size and shape of the transition is significantly affected by the addition of excess Ni content. It is seen that the cooling curves of \( C_p(T) \) demonstrate a much pronounced peak near the martensitic transition temperature \( (T_m) \) than that of the heating curves. It is well known that specific heat is a sensitive probe for the phase transitions involving changes in entropy. The specific heat jump \( (\Delta C_p) \) near the transition can be estimated by subtracting a smooth background far away from the transition, which allows us to evaluate the corresponding entropy change \( (\Delta S) \) using \( \Delta S \approx \Delta C_p/T \) [9]. It is evident that the entropy change near \( T_m \) is found to reduce gradually with increasing Ni content. These findings imply that a small amount of excess Ni in the TiNi alloy not only decreases the martensitic transition temperature, but also weakens the driving force for the transition.

### 3.4. Thermal conductivity

Fig. 6 illustrates the temperature-dependent thermal conductivity data, \( \kappa(T) \) of parent and Ni-rich TiNi alloys. The value of thermal conductivity of the parent TiNi at room temperature is

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_s ) (K)</th>
<th>( A_s ) (K)</th>
<th>( E_F ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti50Ni50</td>
<td>310.3</td>
<td>317.3</td>
<td>2.11</td>
</tr>
<tr>
<td>Ti49.6Ni50.4</td>
<td>280.5</td>
<td>285.4</td>
<td>2.04</td>
</tr>
<tr>
<td>Ti49.3Ni50.7</td>
<td>244.5</td>
<td>253.3</td>
<td>1.89</td>
</tr>
<tr>
<td>Ti49Ni51</td>
<td>174.8</td>
<td>185.0</td>
<td>1.66</td>
</tr>
<tr>
<td>Ti48.7Ni51.3</td>
<td>–</td>
<td>–</td>
<td>1.54</td>
</tr>
<tr>
<td>Ti48.4Ni51.6</td>
<td>–</td>
<td>–</td>
<td>1.53</td>
</tr>
</tbody>
</table>
about 17 W/m K, comparable to that of the reported value for Ti50Ni50 [27]. Thermal hysteresis between the heating and cooling curves of the TiNi alloys with $x \leq 1.0$ is clearly visible near the martensitic transition temperature. It is evident that $k(T)$ has a much more pronounced anomaly near $T_m$ in the heating cycle than that in the cooling, in contrast to the electrical resistivity and specific heat data (Figs. 1, 2 and 5). It is also seen that $k(T)$ of Ti50Ni50 exhibits a relative change in $k$ ($\Delta k/k$) of about 40% during the martensitic transition in the heating. The value of $\Delta k/k$ is found to increase to about 50% for $x = 0.4$ sample, and then decrease for further addition of Ni content with $\Delta k/k \sim 30\%$ and 10% for $x = 0.7$ and $x = 1.0$, respectively. It should be noted here that the magnitude of $\Delta k$ depends on the heating rate of the measurements, as the internal friction ($Q^{-1}$) of the TiNi-based alloys is directly proportional to the cooling/heating rate [28]. Thus, the heating rate of the present thermal conductivity measurement was kept constant at 0.5 K/min for the Ni-rich TiNi-based alloys, the same as in the study on the Cu-substituted TiNi alloys [8].

Since the thermal conductivity data give valuable information about different scattering processes of thermal carriers, we thus

![Fig. 5. Measured specific heat data, $C_p(T)$ of the Ti50Ni50, Ti49.6Ni50.4, Ti49.3Ni50.7 and Ti50Ni51 alloys in the cooling and heating cycles.](image)

![Fig. 6. Temperature-dependent measured thermal conductivity, $k$ of (a) Ti50Ni50 and (b) Ti49.6Ni50.4 alloys in the cooling and heating cycles along with their lattice and electronic thermal conductivity ($k_L$ and $k_e$) during heating process (y-axis in left panels), and (c–f) total, lattice and electronic thermal conductivity data of the Ti49.3Ni50.7, Ti48.7Ni51.3, Ti48.5Ni51.3 and Ti48.8Ni51.3 alloys (y-axis in right panel).](image)
have an opportunity to investigate the interplay between charge and lattice carriers in these Ni-rich TiNi alloys. In general, the total thermal conductivity of the metal can be expressed as a sum of electronic thermal conductivity, $k_e$ and lattice thermal conductivity, $k_l$. The electronic contribution of these alloys can be calculated by using the Wiedemann–Franz law: $k_eT/L_e$, where $\phi$ is the dc electrical resistivity in heating process and $L_e = 2.45 \times 10^{-8}$ W K$^{-2}$ is the Lorenz number (Fig. 6). Lattice thermal conductivity, $k_l$, of the parent and Ni-rich TiNi alloys in the heating cycle is estimated by subtracting the $k_e$ to the total thermal conductivity, which illustrated in Fig. 6. It is found that the T-dependent electronic thermal conductivity tends to follow the total thermal conductivity in the entire temperature range except near $T_m$, similar to that the observation in the Cu-substituted TiNi alloys [8,9]. From this analysis, it is apparent that the anomalous jump in $k$ near $T_m$ is mainly due to the change in lattice thermal conductivity.

The possible origin for the observed sharp anomalous feature in $k$ of the TiNi-based alloys cannot be simply explained by the modifications in electron or phonon scattering processes. However, the phonons may play a crucial role for the anomalous features near the martensitic transition in the thermal conductivity of these alloys (Fig. 6). It is worth to mention here that both specific heat and thermal conductivity showed anomalous peaks in the charge-density-wave materials [29,30], where the soft phonon modes associated with the Kohn anomaly were suggested as the possible origin for the observed anomalous feature. In fact, earlier band calculations suggested that the strong coupling between phonons and the nested electronic states at the Fermi surface is due to the change in lattice thermal conductivity.

Therefore, we can conclude that the modifications in Fermi energy and electronic structures strongly affect the martensitic transition in the Ni-rich TiNi alloys and the alteration in phonon spectra also play an important role for the anomalous features in their thermoelectric transport properties.

4. Conclusion

The thermal and transport properties of Ni-rich TiNi shape memory alloys $\text{Ti}_{50-x}\text{Ni}_{50+x}$ $(x = 0.0–1.6$ at%) were investigated to probe the martensitic transition characteristics. It is found that substitution of excess Ni into Ti sites of $\text{Ti}_{50}\text{Ni}_{50}$ alloy $(x \leq 1.0)$ has resulted in a significant reduction in martensitic transition temperature. Such a finding is apparently due to the weakening of the driving force for the martensitic transition, as the change in entropy near the transition decreases with increasing Ni content. Whereas the features of the strain glass state start to appear in the $\rho(T)$ characteristics of the alloys with $x \geq 1.3$, the signature of martensitic transformation vanishes. A visible phonon drag feature below 50 K in the measured Seebeck coefficient, $S(T)$ of the Ni-rich TiNi alloys shows a typical metallic diffusive behavior with holes as the majority carriers. From the high-temperature $S(T)$ data in the B2 phase, the estimated Fermi energy of these alloys is found to reduce with Ni content to $\sim 1.5$ eV ($\text{Ti}_{48.5}\text{Ni}_{51.5}$) from $\sim 2.1$ eV ($\text{Ti}_{50}\text{Ni}_{50}$). Finally, a pronounced anomalous feature in thermal conductivity at the $B19' \rightarrow B2$ transition was observed for the slightly Ni-rich TiNi alloys $(x \leq 1.0)$, due to the change in lattice thermal transport near the transition. The current investigation demonstrates a strong correlation between electron and phonon degrees of freedom at the martensitic transition in the Ni-rich TiNi alloys, which in turn significantly affects the anomalous features in their thermal and transport properties.

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References


