Cu-substitution effect on thermoelectric properties of the TiNi-based shape memory alloys

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We have studied the effects of Cu substitution on thermoelectric properties of Ti50Ni50−xCu, (0 ≤ x ≤ 30 at. %) shape memory alloys by means of electrical resistivity (ρ), Seebeck coefficient (S), and thermal conductivity (κ) measurements. From the electrical resistivity and Seebeck coefficient studies, it is found that the Cu substituted TiNi alloys show a metallic nature in the entire temperature range. However, thermal hysteresis behavior was observed in all the TiNi-based alloys near martensitic transition, which confirms the first order phase transition. Transformation starting temperature of B19′ martensite (M0) is found to be decreased with increase in Cu substitution (x > 5), whereas that of B19 martensite (M′0) increased gradually with Cu content, and the thermal hysteresis behavior becomes weaker upon substitution of Cu. It is also found that the separation between B19 and B19′ phases in the 7.5% Cu doped TiNi alloy is clearly evident in the Seebeck coefficient measurement, which is not seen in the resistivity data. Finally, analysis of thermal conductivity reveals that the anomalous feature in κ at the B19 → B19′ transformation for 7.5, 10, and 15% Cu-substituted TiNi alloys which can be mainly attributed to the electronic contribution, while a large anomalous peak observed at the B19 → B2 transformation in the warming process is due to change in the lattice thermal conductivity. The relative change in thermal conductivity (Δκ/κ) near martensitic transformation is found to be increased with increase in Cu content, reaches a giant value of 200% for 10% Cu-substituted TiNi alloy and then starts to decrease with further Cu substitution. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4807397]

I. INTRODUCTION

Ti50Ni50 (TiNi) and TiNi-based shape memory alloys have attracted many attentions due to their unique properties of shape memory effect and superelasticity associated with the thermoelastic martensitic transformation (MT).1,2 It has been well known that the TiNi-based alloys undergo a first order phase transition from high temperature cubic austenitic phase (B2) to a low temperature monoclinic martensitic phase (B19′), and the transformation temperature is very sensitive to the thermo-mechanical treatment and alloying.3–7 These alloys are of significant interest due to the fascinating underlying mechanisms, which drive the martensitic transition and the associated changes in their electronic structure and phonon spectrum. Appropriate thermo-mechanical treatment or doping with a third element can change the transformation sequence into two-stage transformation, i.e., from B2 to intermediate rhombohedral R phase and then to B19′ upon cooling in the TiNi alloy.7 It has been reported that a small amount of structural disorder may also affect the R phase stability which can be understood in terms of Fermi-surface nesting.8,9 The lattice anomalies in the phonon dispersion relation, and the interplay between the phonon softening and electronic structure are of particular interest in the TiNi.10–12 The electronic band structure studies have confirmed that these electronic instabilities are in the form of singularities in the density of states (DOS),13,14 i.e., a sharp variation or a peak around the Fermi level (EF) as well as the Fermi surface nesting.8,11,15 In general, such electronic instabilities tend to cause significant variations in the physical properties and also lead to crystallographic transition or distortion as a result of lattice instability. Therefore, the electronic effects associated with changes in chemical composition or alloying of a third element in the TiNi alloy may play a crucial role on the martensitic transition.

The interplay between electronic and disorder effects on the soft phonon instabilities is of great importance to understand the mechanism of MT transformation and its micro/macrosopic behavior of the physical properties. Recently, first principle investigations have made great progress in the shape memory alloys. Particularly, Huang et al.16 have studied the TiNi alloy using density functional theory (DFT) and predicted the stable crystal structure with monoclinic angle of 107° corresponds to B33 structure, instead of the B19′, which was confirmed by experimental studies.1–6 Very recently, the electronic structure and mechanical properties of Cu substituted TiNi (Ti50Ni50−xCu, x = 0–25 at. %) shape memory alloys have been investigated using DFT by Teng et al.17 It was found that the calculated formation energies and equilibrium lattice constants increase with increase in Cu concentration. The tendency of their martensitic transformation behaviors was also deduced upon Cu substitution, where a two-stage MT, B2 → B19 → B19′, would take place with Cu content in the range of 6.25% and 18.75%. Moreover, it is revealed that the softening of both shear constants (Cij) and anisotropy factors (A) in the Cu doped

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TiNi alloys led to a one-stage MT of B2-B19′ and B2-B19 for Cu content ≤6.25% and ≥18.75%, respectively. There are many reports on the effects of ternary alloying elements on martensitic transition of TiNi and shape memory characteristics in the metallurgical point of view, however very few studies on thermoelectric properties such as Seebeck coefficient and thermal conductivity. In addition to electrical resistivity, the Seebeck coefficient can be more effectively used to probe the changes in DOS across the martensitic transition. Lee et al. have reported a sharp variation in Seebeck coefficient near the phase transition and also suggested that the presence of a peak near the Fermi level may be the cause of the lattice instability in the TiNi.

Among the third element substitution in the TiNi alloy, the element Cu has a unique nature that it can be substituted for Ni up to 30 at. % and still exhibits shape memory effects. Nam et al. proposed a phase diagram regarding Cu content versus transformation temperatures, $M_s$ (B19′) and $M_t$ (B19), of Cu doped TiNi alloys with Cu content from 5% to 20%. This investigation was done using techniques such as electrical resistivity, differential scanning calorimetry (DSC), and constant load thermal cycling tests. Recently, we investigated electrical and thermal transport studies on 10% Cu and 1.5% Fe substituted TiNi alloys. In this study, a clear thermal hysteresis behavior between warming and cooling condition of resistivity, Seebeck coefficient, and thermal conductivity measurements was observed in the undoped and doped TiNi alloys, which indicated first order martensitic phase transition and also found to be two-stage transformation. The anomalous features in the measured physical properties suggested that the modifications in the Fermi surface and strong electron-phonon interaction may play important roles at the martensitic transition of the TiNi-based alloys. In the present work, we have carried out a comprehensive study of thermoelectric properties of the Cu substituted TiNi alloys, namely Ti$_{50}$Ni$_{50-x}$Cu$_x$ ($x = 0–30$ at. %) with different Cu content. Based on these investigations, we have tried to understand the physical significance of two-stage transformation in the Cu doped TiNi shape memory alloys and also revisited the phase diagram proposed by Nam et al. The transition temperatures of MT are determined by more sensitive probes such as Seebeck coefficient and thermal conductivity studies. It is found that the separation between the transitions of two-stage MT in the 7.5% Cu doped TiNi was only seen in the Seebeck coefficient studies with separation of about 15 K. Besides, a large anomalous peak in thermal conductivity was observed at the B19 $\rightarrow$ B2 transformation in the warming process, which increases significantly with Cu substitution and reaches a giant value of $\Delta \rho/\rho$ $\sim$200% for 10% Cu doping, and then reduces for further Cu substitution.

II. EXPERIMENTAL DETAILS

Polycrystalline ingots of Ti$_{50}$Ni$_{50-x}$Cu$_x$ ($x = 0–30$ at. %) shape memory alloys were prepared using vacuum arc re-melter in which high purity titanium, nickel, and copper were re-melted at least six times in high purity Ar atmosphere. As-melted ingots were homogenized and then hot-rolled at 1173 K to the plates of about 2 mm thicknesses by using a rolling machine. Subsequently, the plates were solution treated at 1173 K for 1 h and then water-quenched; for more details see Ref. 22. Electrical resistivity measurement of the TiNi-based alloy samples was performed using a standard four-point contact method. Seebeck coefficient and thermal conductivity measurements of the samples were simultaneously carried out using a direct heat pulse technique over the temperature range of 10–400 K. Further details about these measurement techniques can be found elsewhere.

III. RESULTS AND DISCUSSION

A. Electrical resistivity

Temperature-dependent electrical resistivity, $\rho(T)$, of the Ti$_{50}$Ni$_{50-x}$Cu$_x$ ($0 \leq x \leq 30$ at. %) alloys during cooling and warming process is shown in Figs. 1–3. Room temperature resistivity of the TiNi alloy was found to be reduced gradually with Cu substitution until up to 10%, from about 86 $\mu$Ω cm to 67 $\mu$Ω cm, and then increased for 15% Cu doping ($\sim$122 $\mu$Ω cm) and again started to reduce for further substitution of Cu. On the other hand, the value of residual resistivity of the Cu substituted TiNi alloys is found to be increased more than double than that of the parent TiNi ($\sim$25 $\mu$Ω cm), inferring the presence of impurity scattering in the substituted alloys. However, the value of residual resistivity of the parent TiNi alloy is considerably lower than that of previously reported value, suggesting the highly ordered nature of the sample. Moreover, upon cooling from 400 K, the resistivity shows a sharp rise followed by a sudden fall in the form of two well-defined peaks in the parent TiNi alloy, as seen in the inset of Fig. 1(a). With further decrease in temperature, the resistivity of the TiNi alloy decreases, which represents a typical metallic behavior, as
observed in Ni-Mn-Ga shapes memory alloys. It is noted that two peaks are clearly seen in the $q(T)$ curve at 298 K and 292 K, corresponding to $B_2 \rightarrow R$ and $R \rightarrow B_19^0$ transformation, respectively (Fig. 1(a)). However, the previous reports on resistivity behavior of the near-equatomic samples showed only a single peak in the cooling curve as result of the transformation from the high-temperature austenite phase ($B_2$) to a low-temperature martensite phase ($B_19^0$). It is also possible that the intermediate phase ($R$, rhombohedral) appears before $B_19^0$ for certain compositions and heat treatments. The starting/finishing temperatures for this intermediate R phase as well as martensite and austenite phases have been represented by $R_s/R_f$, $M_s/M_f$ and $A_s/A_f$, respectively, as shown in Fig. 1. On the other hand, the warming curve of $\rho(T)$ shows only one peak in the parent TiNi, which occurs at a higher temperature of around 326 K. Such a finding suggests that the reverse transformation occurs only in one-stage, i.e., directly from $B_19^0$ to $B_2$.

The shape of the $\rho(T)$ curves is strongly dependent on the substituted Cu concentration, which can be clearly seen in Figs. 1–3. In 5% Cu substituted TiNi (Fig. 1(b)), the $\rho(T)$ curve on cooling shows only one minimum, which corresponds to $M_s$ (transformation starting temperature of $B_19^0$ phase), whereas in the alloys with 10 and 15% Cu, the $\rho(T)$ has two minima (Fig. 2), one of which at higher temperature corresponds to $M'_s$ (transformation starting temperature of $B_19$ phase) and the other to $M_s$. Here, the $\rho(T)$ curve of the alloys on warming process changes in a similar manner to that of the cooling process, i.e., the $\rho(T)$ curve has only one maximum for 5% Cu doped TiNi alloy, whereas it has two maxima for 10 and 15% Cu doped TiNi alloys, one of which at lower temperature corresponds to $A_s$ and the other corresponds to $A'_s$ (Fig. 2). Here, $M'_s$ and $A'_s$ are the starting temperature of $B_19^0 \rightarrow B_19$ and $B_19 \rightarrow B_2$ transformation, respectively. For the TiNi alloys with >15% Cu doping, the $\rho(T)$ curve has only one minimum at $M'_s$ and $A'_f$ on cooling and heating, respectively, as seen in Fig. 3.

In order to elucidate the correlation between the three phases ($B_2$, $B_19$, and $B_19^0$) in the Cu doped TiNi alloys, the values of $M'_s$ and $M_s$ are plotted against Cu content. It can be seen clearly that there is no clear separation between $M'_s$ and $M_s$ in the alloy with 7.5% Cu content. However, this separation was estimated to be about 7 K by Nam et al. using DSC measurements. Whereas the separation is seen clearly in the 10% Cu-substituted TiNi alloy, which found to increase with increase in Cu content until about 15%. The value of $M_s$ is found to be increased slightly with doping of 5% Cu and then it decreases significantly for further Cu doping, whereas the value of $M'_s$ is found to be increased slightly with increase in Cu content. The estimated thermal hysteresis of the Cu doped TiNi-based alloys is also plotted against Cu content. The hysteresis temperature of Cu doped TiNi alloys is found to be less than that of the parent TiNi alloy (~35 K), and the hysteresis behavior becomes very weak (~5 K) for 30% Cu content. In Sec. III B, the evaluation of two-stage MT will be further explored using highly sensitive probe of Seebeck coefficient.

### B. Seebeck coefficient

Temperature-dependent Seebeck coefficient, $S(T)$, of the Ti$_{50}$Ni$_{50-x}$Cu$_x$ alloys in the cooling and warming process is illustrated in Figs. 4–6. The measured Seebeck coefficient of the all TiNi-based alloys was found to be positive in the entire temperature range under investigation, despite a small negative phonon drag contribution below 30 K for $x = 15$ and 20, suggesting that the majority charge carriers are holes. The room-temperature $S$ values vary from 1 to 20 $\mu$V/K, which shows a strong variation as a function of Cu concentration. The maximum $S$ value (~20 $\mu$V/K) at room temperature (RT)
was obtained for the substitution level of \( x = 5 \), and then the \( S \) value gradually reduces to \( \sim 1 \mu V/K \) for further substitution of Cu. In general, both electrons and holes contribute to the thermoelectric transport in the electrically conducting materials. In the present case of Ti50Ni50\(_x\) Cu\(_x\) alloys, the increase in the number of electrons, which has a higher mobility than the holes, may lead to the observed reduction in the \( S \) value for the higher Cu content (\( x > 5 \)). The \( S(T) \) characteristics in the parent TiNi alloy shows a sharp rise in both cooling and warming conditions at 305 K and 340 K, respectively, with a temperature hysteresis of about 35 K (Fig. 4). It is found that the Seebeck coefficient shows a sharp dip on cooling at 306 K, which indicates the presence of the intermediate R phase. The 5% Cu substituted TiNi alloy has only one minimum, which corresponds to \( M_s \) (Fig. 4(b)), whereas in the alloys with 7.5, 10, and 15% Cu, the \( S(T) \) curves show two anomalous features due to two-stage MT, B2\( \rightarrow \)B19\( \rightarrow \)B19\(_0\) (Fig. 5), one of which at higher temperature corresponds to \( M'_s \) and the other to \( M_s \). These observations are quite consistent with earlier report by Nam \textit{et al.}\textsuperscript{20} The occurrence of the intermediate tetragonal B19 phase in the Cu doped TiNi alloys can be attributed to the softening of both shear elastic constants and anisotropy factors upon substitution of Cu.\textsuperscript{17} For higher Cu content (\( x > 15 \)), the \( S(T) \) has again only one minimum (Fig. 6), which is also consistent with the resistivity data (Fig. 3). In Fig. 6, on the cooling process, the peak in the \( S(T) \) corresponds to the starting temperature of the B2\( \rightarrow \)B19 transition (\( M'_s \)), while the change of curvature of \( S(T) \) below the peak denotes the end of the transition (\( M'_0 \)). On the other hand, on the heating, the change of curvature below the peak denotes the start of the B19\( \rightarrow \)B2 transition (\( A'_0 \)) and the peak signifies the end of the transition (\( A'_s \)). Below the transition temperatures, the \( S(T) \) curves of the Cu doped TiNi alloys follow a typical metallic diffusive behavior, and a visible hump below 50 K is also noticeable, as indicated by the arrows in Figs. 1–6. This low-temperature feature in the Cu doped TiNi alloys is most likely due to the phonon drag effect, which is found to be suppressed in earlier report on TiNi presumably due to the disorders.\textsuperscript{5} However, the nature of phonon drag effect is found to be altered for high Cu concentration (\( x \geq 20 \)) doping in the TiNi alloy (Fig. 6), and this new feature is found to be quite similar to that of the phonon drag thermopower of the metallic copper, Cu.\textsuperscript{26} It is also noticed that the...
measured $S(T)$ for the Cu doped TiNi alloys are quite linear at higher temperatures (in the B2 phase). For ordinary metals, the Seebeck coefficient is expected to be linear with temperature and can be expressed by Mott’s formula, $S = \frac{\pi^2 k_B^2}{3e} T = b T$, assuming a one-band model with an energy-independent relaxation time. Here, $E_F$ is Fermi energy and $k_B$ is Boltzmann constant. From fitting of the data to the above equation in the high-$T$ austenitic phase, we have estimated the value of Fermi energy ($E_F$) for the parent and Cu doped TiNi alloys. The estimated Fermi energy is found to be increased gradually from 1.7 eV (for Ti50Ni50) to 3.0 eV (for Ti50Ni35Cu15), which is in good agreement with metallic nature of the TiNi alloys, and then started to reduce for further Cu doping ($x > 15$), which is displayed in Fig. 7. Therefore, the doping of Cu in Ni sites of TiNi alloy may be resulted in a change in $E_F$ and its electronic properties, which in turn has a strong influence on the martensitic transition.

The Seebeck coefficient is known to be very sensitive to the small changes in the position of Fermi energy ($E_F$) across the DOS. The sharp variations in the $S$ near martensitic transition indicate a significant modification in the DOS of the Fermi surface. Another important finding is that the prominent hysteresis feature in the TiNi-based alloys is found to be gradually reduced from 35 K to 5 K for 30% Cu doping, close to that of the reported value for a dense TiNi alloy. In all these shape memory alloys, the presence of a peak near $E_F$ and Fermi surface nesting have been well established through both experimental and theoretical investigations. However, the exact driving force for the observed anomalies near Fermi surface is still an intriguing issue that needs further investigations. As discussed above, the anomalous features in the measured Seebeck coefficient are mainly due to the modifications in the Fermi surface as these TiNi-based alloys undergo martensitic transitions. The peak in the DOS located slightly below $E_F$ as predicted by the band structure calculations may be a contributing factor. It is also well known that the peaks in the DOS near $E_F$ may cause lattice instabilities, which will lead to possible structural transitions.

In order to demonstrate the effect of Cu substitution on the martensitic-austenitic transformation and hysteresis behavior, we have plotted the temperature values of $M_s$, $M_f$, and thermal hysteresis against the Cu content, as shown in Figs. 8(a) and 8(b), respectively. The separation between $M'_s$ and $M_s$ is found to be clearly noticeable with a value of 15 K for 7.5% Cu doped TiNi alloy and increased with further increase in Cu content up to 15% (Fig. 8(a)). Hence, the temperature over which the B19 phase is stable becomes wider with increasing Cu content, which consistent with both theoretical and experimental observations. The estimated temperature of hysteresis behavior of the TiNi alloy was found to be gradually decreased with the substitution of Cu from 35 K to 5 K (Fig. 8(b)). It is seen that the substitution of Cu results in a change in $E_F$ and electronic properties of the TiNi alloy, which has a strong influence on the martensitic transition. The observed superior stability of the martensite B19 phase and the weakening of hysteresis behavior upon doping of Cu in the TiNi alloy may be due to the increase in the DOS at $E_F$, which consequently results in a more stable Ti50Ni50-Cu alloy system. However, the contribution from both electronic and lattice order parameters are essential for understanding the physical properties of the Cu-substituted TiNi alloys, which will be further discussed as we analyze the thermal conductivity data in Sec. III C.

C. Thermal conductivity

Temperature-dependent total thermal conductivity, $\kappa(T)$, of parent TiNi alloy in the warming and cooling process is shown in Fig. 9. The value of thermal conductivity of the parent TiNi alloy at RT is about 14 W/m K, which is comparable to that of the reported value for a dense TiNi alloy. Thermal hysteresis between warming and cooling near martensitic transition temperature ($T_m$) is seen clearly with a significant hysteresis behavior, as observed in both the electrical resistivity and Seebeck coefficient measurements. It is

FIG. 7. Estimated Fermi energy ($E_F$) vs Cu content of the Cu doped TiNi alloys from high temperature Seebeck coefficient data.

FIG. 8. (a) The value of $M'_s$ and $M_s$ vs Cu content and (b) temperature of hysteresis behavior vs Cu content from Seebeck coefficient measurements.
also noticed that the thermal conductivity has a much pronounced anomaly in the warming than in the cooling process, in contrast to the electrical resistivity data. Since the thermal conductivity measurements can provide valuable information about different scattering processes of thermal carriers, here we have an opportunity to probe the interplay between thermal carriers of lattice and charge degrees of freedom in the TiNi. In general, the total thermal conductivity of the metal can be expressed as a sum of electronic thermal conductivity, \( \kappa_e \), and lattice thermal conductivity, \( \kappa_L \), terms. The electronic contribution was estimated by using the Wiedemann-Franz law: \( \kappa_e \rho / T = L_0 \), where \( \rho \) is the dc electrical resistivity in the warming process and \( L_0 = 2.45 \times 10^{-8} \text{W} \cdot \text{K}^{-2} \cdot \text{m}^{-1} \) is Lorentz number (Fig. 9). The lattice thermal conductivity, \( \kappa_L \), for the TiNi alloy in warming process is calculated by subtracting the electronic \( \kappa_e \) to total \( \kappa \), which is also shown in Fig. 9. It is found that the electronic thermal conductivity roughly follows the total thermal conductivity in the entire temperature range except near \( T_m \). From these observations, it is clear that the anomalous jump in \( \kappa \) near \( T_m \) is due to the change in lattice thermal conductivity during the warming process, but not due to electronic contribution. However, the anomaly in \( \kappa \) during cooling process is mainly due to the change in the electronic thermal conductivity. Moreover, the value of \( \kappa_L \) below 50 K is found to be increased rapidly with temperature, which follows the kinetic equation of the lattice thermal conductivity given by \( \kappa_L = C_v \nu / l \), \(^{28}\) where \( C_v \) is the phonon specific heat, \( \nu \) represents the phonon drift velocity, and \( l \) is the mean free path. From this study, it is found that the phonon specific heat has the strongest temperature dependence \( (C_v \propto T^3) \) at low-\( T \) than that of other physical parameters in the TiNi-based alloys.\(^{22}\)

Temperature-dependent lattice thermal conductivity, \( \kappa_L(T) \), of the Cu doped TiNi, Ti\textsubscript{50}Ni\textsubscript{50}Cu\textsubscript{x}, alloys in the warming process is displayed in Fig. 10. The \( \kappa_L(T) \) value of room-temperature thermal conductivity of the presently investigated TiNi-based alloys lies between \(~4 \text{ W/m K} \) and \(~7 \text{ W/m K} \), strongly affected by substitution of Cu in the Ni sites of TiNi alloy. It is also noticed that the value of \( \kappa \) of the parent TiNi exhibits a distinct jump with \( \Delta \kappa/\kappa \sim 34\% \) near the martensitic transition, which is found to be affected upon the substitution of Cu. In order to further analyze Cu substitution effect on the anomalous peak near \( T_m \), we plot the relative change in \( \kappa \) \( (\Delta \kappa/\kappa) \) against the Cu content, which is shown in the inset of Fig. 10. The value of \( \Delta \kappa/\kappa \) is found to be increased linearly with Cu content up to 10\% and then decreased gradually with further substitution of Cu. It should also be mentioned here that the magnitude of \( \Delta \kappa \) depends on the heating rate of the measurements, a behavior quite similar to the damping capacity exhibited in the MT of TiNi-based alloys. It is well known that TiNi-based shape memory alloys possess a high level of internal friction, \( Q^{-1} \), in the temperature range of a thermo-elastic martensitic transformation.\(^{2} \) Delorme \textit{et al.} suggested that the value of \( Q^{-1} \) is proportional to the cooling/heating rate (the forward/reverse transformation rate).\(^{29}\) Therefore, the heating rate of the thermal conductivity measurements was kept constant at 0.5 K/min for all samples in this study.

Furthermore, the possible origin for the observed colossal anomalous peaks in \( \kappa \) of these TiNi-based alloys cannot be simply explained by the changes in electron or phonon scattering process. From Figs. 9 and 10, it seems that the phonons may play an important role for these observed anomalous peaks in the thermal conductivity of the TiNi-based alloys. It is also worth mentioning here that both specific heat and thermal conductivity shows anomalous peaks in the charge-density-wave (CDW) materials.\(^{30,31}\) The appearance of Kohn anomaly and the excess heat carried by soft phonons were suggested as possible origins for such an anomalous feature in the thermal properties of these materials. In general, it is expected that the magnitude of the

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**FIG. 9.** Temperature-dependent total thermal conductivity \( \kappa(T) \) of parent TiNi alloy in cooling and warming process along with the electronic and lattice thermal conductivity in the warming.

**FIG. 10.** Temperature-dependent lattice thermal conductivity \( \kappa_L(T) \) of the Ti\textsubscript{50}Ni\textsubscript{50}Cu\textsubscript{x} alloys in the warming process. Inset shows Cu content dependent relative change in the \( \kappa \) value \( (\Delta \kappa/\kappa) \) near \( T_m \) of the Cu doped TiNi-based alloys.
anomalous peak in the thermal conductivity should be proportional to that of specific heat if both the phonon drift velocity and mean free path are not strongly influenced by the transitions as per the equation $\kappa = C_{\text{p}}v_f$. However, the relative change in lattice thermal conductivity near $T_m$ is found to be as large as 200% for the 10% Cu substituted TiNi alloy, which seems to be unusual. From the inset of Fig. 10, it is noted that the tendency of the relative change in $\kappa$ with respect to the Cu concentration is quite similar to that of Cu-dependent the estimated Fermi energy from the high-$T$ Seebeck coefficient data (Fig. 7), which confirms the correlation between phonon and electronic structures in the TiNi-based systems.\textsuperscript{10–12} Finally, the observed two-stage martensitic transformation for the Cu doped TiNi-based alloys with 7.5–15% Cu content can be attributed to the softening of both shear constants and anisotropy factors,\textsuperscript{17} and the doping of Cu in the TiNi alloy also led to the change in $E_F$ and electronic properties, which in turn has a strong influence on martensitic transformation.\textsuperscript{20,22}

**IV. CONCLUSIONS**

Effects of Cu substitution on thermoelectric properties of TiNi-based shape memory alloys, namely Ti$_{50}$Ni$_{50-x}$Cu$_x$ (0 $\leq x \leq$ 30 at.%) were investigated using the electrical resistivity, Seebeck coefficient, and thermal conductivity measurements. From the studies of electrical resistivity and Seebeck coefficients, it is found that the Cu-substituted TiNi alloys show a metallic nature in the entire temperature range. The starting temperature of B19' martensitic transition ($M_s$) is found to be decreased gradually for substitution of Cu ($x > 5$), whereas the starting temperature of B19 martensitic transition ($M'_s$) increased gradually with Cu content. Hence, the temperature range over which the intermediate B19 martensite phase is stable becomes wider with increase in Cu content. From the electrical resistivity and Seebeck coefficient studies, it is found that the hysteresis behavior associated with the martensitic-austenitic transformation becomes gradually weaker with increasing of Cu content. It is also found that the separation between the B19 and B19' phases of the 7.5% Cu doped TiNi alloy is clearly noticeable in the Seebeck coefficient measurement which estimated to be about 15 K, and it is found to be increased gradually for further Cu doping up to 15%. Analysis of thermal conductivity of the Cu-substituted TiNi alloys reveals that the anomalous feature in $\kappa$ at the B19 $\leftrightarrow$ B19' transformation can be mainly attributed to the electronic contribution, whereas a large anomalous peak observed at the B19 $\rightarrow$ B2 transformation in the warming process is due to the change in lattice thermal conductivity. The relative change in $\kappa$ ($\Delta\kappa/\kappa$) is found to be increased significantly with Cu substitution and reached to a giant value of 200% for 10% Cu doping and then started to decrease for further Cu substitution. The resemblance of Cu concentration dependent relative change in the thermal conductivity and the estimated Fermi energy from high-$T$ Seebeck coefficients indicates the correlation between phonon and electronic structures in the TiNi-based system.

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