Experimental study of the titanium nickelide thermophysical properties complex

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Abstract. The article presents new experimental data on the thermal diffusivity ($\alpha$), thermal conductivity ($\lambda$), heat capacity ($c_p$) and linear thermal expansion coefficient ($\alpha$) of titanium nickelide (56.6 wt. % Ni, 43.4 wt. % Ti). The temperature interval from 293 to 872…962 K has been investigated by laser flash technique, method of differential scanning calorimetry and dilatometric method. The estimated errors of the received data were 2–4%, 3–5%, 2–3% and $(1.5–2)\times10^{-7}$ K$^{-1}$ for $\alpha$, $\lambda$, $c_p$ and $\alpha$, respectively. The approximation dependences and the reference table of investigated transport, caloric and thermal properties have been obtained.

1. Introduction

Titanium nickelide (TiNi) is the most well-known of the materials with the properties of superelasticity and shape memory. The shape memory effect in metals and alloys is not of only scientific but also of great practical importance; in some cases, its application provides a solution to very complex technical problems. Superelasticity and shape memory effect in TiNi are caused by thermoelastic martensitic transformations in the material and depend essentially on composition, heat treatment, deformation, etc. [1, 2], which makes it extremely interesting to study its physical properties. Alloys in which this effect is manifested with a change of temperature, pressure, or during deformation have unique and practically attractive properties, such as high damping capacity, excellent corrosion resistance, good strength properties, high shape restoring coefficient, as well as high biocompatibility with human body tissues. Thereby, currently titanium nickelide and its alloys are widespread in many industries, mechanical engineering, robotics, aerospace field and others. For example, such alloys are used in fire protection devices, as release of current circuits, for sealing joints of aircraft, submarines and for preventing radiation leakage at nuclear power plants, as well as in the space industry to create self-opening compact antennas. TiNi based alloys are widely used in medicine for the manufacture of implants and corrective devices, including dentistry, orthopedics and vascular surgery.

A lot of theoretical and experimental works have been devoted to the study of the properties of this alloy, but all of them were carried out in a narrow temperature range and were mainly devoted to the study of mechanical and acoustic properties. The experimental information available in the literature on thermophysical properties of TiNi is scarce. We were able to find two works [3, 4] with low temperature (up to 300 K) thermal conductivity measurements and one paper [5], in which the complex of thermophysical properties of titanium nickelide from room temperature to 1100 K was studied. However, the authors investigated alloys with different contents of Ti and Ni in these articles.
In this regard the aim of the present work was an experimental study of transport, caloric and thermal properties of titanium nickelide (56.6 wt. % Ni, 43.4 wt. % Ti) in a wide temperature interval of a solid state, including the region of phase transformation.

2. Experimental methods

The thermal diffusivity ($\alpha$) of investigated TiNi was measured by the laser flash method using an automated experimental installation LFA-427 [6], according to the technique described in detail in [7, 8]. The sample under study had the shape of a cylinder with a diameter of 6 mm and a thickness of 2.5 mm with plane-parallel polished ends. The computational model proposed by Cape and Lehman [9] was used. Corrections for the laser pulse finite duration and its real shape were found in accordance with the procedure [10]. The experiments were carried out in heating-cooling cycles in the temperature range of 293–928 K in a static argon atmosphere (99.992 vol. %). The estimated error in the measurement of $\alpha$ for solid samples on LFA-427, confirmed by experiments with well-studied molybdenum and standard inconel and pyroceram samples, was 2–4%.

The measurements of the heat capacity ($c_p$) of titanium nickelide alloy were carried out by the method of differential scanning calorimetry (DSC). The mass of the measured sample was 260.06 mg. The experiments were performed on DSC 404 F1 calorimeter [11] using platinum crucibles with corundum inserts in the temperature interval of 298–962 K with a heating-cooling rate of 20 K min$^{-1}$ in a flowing argon atmosphere with a purity of 99.992 vol. %. The Ar flow rate was 20 ml min$^{-1}$. The sample of 12Kh18N10T stainless steel weighing 160.13 mg was used as a standard sample for $c_p$. The measurement error of $c_p$ for DSC 404 F1 setup was 2–3%, what was established from the experiments with reference samples of high-purity platinum and sapphire.

The linear thermal expansion coefficient (LTEC, $\alpha$) of TiNi was determined by dilatometric method on DIL-402C apparatus of horizontal type [12] using a holder and a pushrod made of sintered alumina. A detailed description of the measurement technique and processing of the LTEC results were given in [13]. Investigated sample was made in the form of a cylinder 25 mm long and 6 mm in diameter. The measurements were performed in the temperature range of 293–872 K with a furnace heating-cooling rate of 2 K min$^{-1}$ and 30 minutes isothermal holding at maximum temperature in a static helium atmosphere (99.995 vol. %), which was additionally purified by a system for cleaning and drying of inert gases EPISHUR-A 11 SL [14]. The error of the obtained data on $\alpha$, which was verified by experiments with samples of pure platinum (99.93 wt. %) and copper (99.995 wt. %), was $(1.5–2)\times10^{-7}$ K$^{-1}$.

3. Results and discussion

The results of $c_p$ measurements of titanium nickelide (56.6 wt. % Ni, 43.4 wt. % Ti) are presented in figure 1. The experiments have shown that in the high-temperature region an anomalous change in the temperature dependence of the heat capacity was registered. Apparently, it was associated with thermoelastic martensitic transformation occurring in TiNi [2]. As it can be seen from figure 1 a specific heat capacity hysteresis was observed in the heating-cooling cycles, moreover, an anomalous change in $c_p(T)$ occurred only by heating the sample. One can notice that $c_p$ decreases in the temperature range of 520–740 K and reaches a minimum at temperature $T_{\text{ph}} = 667.8$ K, as well as increases in the temperature range of 750–870 K and reaches a maximum at a temperature $T_{\text{m}} = 808.3$ K. It should also be noted that $c_p$ is an effective value in the interval of 520–870 K, which depicts both the intrinsic heat capacity of phases in the alloy and the contribution of the thermal effect of the phase transition. In this situation we can only talk about the value of $c_p$ obtained during heating in the temperature intervals of 298–520 K and 870–962 K. The heat capacity measurements of TiNi, performed in all heating-cooling cycles excluding the phase transformation area, showed good reproducibility of results.

The approximation of $c_p$ experimental data obtained by heating of the sample under study gave the following equations:

$$c_p(T) = 0.201 + 9.37\times10^{-4} T - 8.32\times10^{-7} T^2, \quad 298 \leq T \leq 520 \text{ K},$$  

(1)


\[ c_p(T) = 0.154 + 6.72 \times 10^{-4} T - 3.46 \times 10^{-7} T^2, \quad 870 \leq T \leq 962 \text{ K}, \]  

(2)

where \( T \) is the temperature in K, \( c_p \) is in J (g K)\(^{-1}\). The standard deviations of the experimental data from the approximation dependences (1) and (2) do not exceed 0.13\% and 0.32\%, respectively.

The approximation of \( c_p \) experimental data obtained during the cooling of the sample gave the equation:

\[ c_p(T) = 0.367 + 2.61 \times 10^{-4} T - 1.51 \times 10^{-7} T^2, \quad 435 \leq T \leq 962 \text{ K}. \]  

(3)

The standard deviation of the experimental points from (3) does not exceed 0.20\%.

\[ \alpha(T) = 11.01 - 3.15 \times 10^{-4} T + 2.62 \times 10^{-6} T^2, \quad 293.15 \leq T \leq 686 \text{ K}, \]  

(4)

\[ \alpha(T) = 27.99 - 50.87 \times 10^{-3} T + 40.23 \times 10^{-6} T^2, \quad 686 \leq T \leq 768 \text{ K}, \]  

(5)

\[ \alpha(T) = 1210.99 - 463.93 \times 10^{-2} T + 59.699 \times 10^{-4} T^2 - 255.316 \times 10^{-8} T^3, \quad 768 \leq T \leq 810 \text{ K}, \]  

(6)

\[ \alpha(T) = -4817.99 + 1752.806 \times 10^{-2} T - 211.635 \times 10^{-4} T^2 + 8502.915 \times 10^{-9} T^3, \quad 810 \leq T \leq 852 \text{ K}, \]  

(7)

\[ \alpha(T) = 305.95 - 67.77 \times 10^{-2} T + 390.54 \times 10^{-6} T^2, \quad 852 \leq T \leq 872 \text{ K}, \]  

(8)

where \( \alpha \) is in \( 10^{-6} \text{ K}^{-1} \). The standard deviations of the experimental points from the approximations (4)–(8) do not exceed 2.13, 2.12, 2.13, 2.30 and 2\%, respectively.

The relative expansion recommended values (\( \varepsilon \)) were obtained by integrating the \( \alpha(T) \) curve with the condition that \( \varepsilon(293.15 \text{ K}) = 0 \). The temperature dependence of density \( \rho(T) \) was calculated from \( \varepsilon(T) \) and the density at 293.15 K, which was found from the geometrical dimensions and the mass of the sample. The corresponding approximation equation for the density is presented below:
\[ \rho(T) = 6619 - 0.23 \, T, \quad 293.15 \leq T \leq 872 \, \text{K}, \quad (9) \]

where \( \rho \) is in kg m\(^{-3}\). The standard deviation of the obtained density values from the dependence (9) does not exceed 0.01%.

The experimental data on the thermal diffusivity of TiNi obtained in several heating and cooling cycles were reproduced among themselves within the limits of the estimated measurement errors. It should be noted that on the \( a(T) \) an anomalous changes in properties both during heating and cooling were not observed, in contrast to \( c_p(T) \) and \( a(T) \). The \( a(T) \) function increased monotonically with increasing temperature over the entire range studied. The approximation of \( a \) experimental data gave the following expression:

\[ a(T) = 1.49 + 8.97 \times 10^{-3} \, T - 3.17 \times 10^{-6} \, T^2, \quad 293.15 \leq T \leq 928 \, \text{K}, \quad (10) \]

where \( a \) is in \( 10^{-6} \, \text{m}^2 \, \text{s}^{-1} \). The standard deviation of the experimental points from the equation (10) does not exceed 0.63%.

With allowance for experimental data on \( a \), approximation equations (1)–(3) and (9) for \( c_p \) and \( \rho \), and also the known equation \( \lambda = a \, \rho \, c_p \), the values of the thermal conductivity (\( \lambda \)) of investigated titanium nickelide have been calculated. The thermal conductivity error increases to 3–5% due to \( c_p \) and \( \rho \) errors, which are used in the recalculation of \( a \) to \( \lambda \). The calculated \( \lambda \) data were approximated by a second-degree polynomial:

\[ \lambda(T) = 0.65 + 3.765 \times 10^{-2} \, T - 1.61 \times 10^{-5} \, T^2, \quad 293.15 \leq T \leq 872 \, \text{K}, \quad (11) \]

where \( \lambda \) is in W (m K\(^{-1}\)). The standard deviation of the thermal conductivity data from the approximation equation (11) does not exceed 0.67%.

The recommended values for \( a, \lambda, c_p, \alpha, \varepsilon \) and \( \rho \) of TiNi alloy are presented in the table.

**Table.** The recommended values of titanium nickelide thermophysical properties.

| T, K | \( a, 10^6 \, \text{m}^2 \, \text{s}^{-1} \) | \( \lambda, \text{W} (\text{m K})^{-1} \) | \( c_p, \text{J} (\text{g K})^{-1} \) | \( \alpha, 10^{-6} \, \text{K}^{-1} \) | \( \varepsilon, 10^{-6} \) | \( \rho, \text{kg} \, \text{m}^{-3} \) |
|------|------------------|-----------------|-----------------|------------------|----------------|------------------|
| 293.15 | 3.84 | 10.30 | 0.404 | 11.15 | 0 | 6550 |
| 300 | 3.89 | 10.50 | 0.407 | 11.16 | 76.4 | 6548 |
| 350 | 4.24 | 11.85 | 0.427 | 11.23 | 635.9 | 6538 |
| 400 | 4.57 | 13.13 | 0.443 | 11.31 | 1199.2 | 6526 |
| 450 | 4.88 | 14.33 | 0.454 | 11.40 | 1766.9 | 6515 |
| 500 | 5.18 | 15.45 | 0.462 | 11.51 | 2339.8 | 6504 |
| 550 | 5.46 | 16.49 | 0.465 | 11.63 | 2918.4 | 6493 |
| 600 | 5.73 | 17.45 | 0.469 | 11.77 | 3503.5 | 6482 |
| 650 | 5.98 | 18.32 | 0.473 | 11.92 | 4095.6 | 6470 |
| 700 | 6.21 | 19.12 | 0.476 | 12.10 | 4695.6 | 6459 |
| 750 | 6.43 | 19.84 | 0.478 | 12.47 | 5309.1 | 6447 |
| 800 | 6.63 | 20.47 | 0.479 | 13.07 | 5947.1 | 6435 |
| 850 | 6.82 | 21.03 | 0.480 | 12.08 | 6582.8 | 6422 |
| 872 | 6.90 | 21.24 | 0.480 | 11.95 | 6846.3 | 6417 |
| 900 | 6.99 | 21.50 | 0.480 | — | — | — |
| 928 | 7.08 | 21.73 | 0.479 | — | — | — |
| 950 | — | — | 0.479 | — | — | — |
| 962 | — | — | 0.479 | — | — | — |
Conclusion
New reliable experimental data on the thermal diffusivity, thermal conductivity, heat capacity and linear thermal expansion coefficients of titanium nickelide alloy (56.6 wt. % Ni, 43.4 wt. % Ti) in the temperature interval of 293–872…962 K have been obtained for the first time. Changes in the temperature dependences of the heat capacity and linear thermal expansion at thermoelastic martensitic transformation have been determined. It has been found that the thermal diffusivity coefficient of TiNi increased monotonically with the temperature without any anomalous changes at solid-phase martensitic transformation. The approximation dependences and the table of recommended values of studied transport, caloric and thermal properties have been developed.

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