International Journal of Thermophysics, Vol. 22, No. 6, November 2001 (© 2001)

Thermal and Electrical Properties of Titanium Between 300 and 1900 K

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Received May 11, 2001

The specific heat capacity and electrical resistivity of titanium were measured by a subsecond pulse-heating method. Specimens were in the form of a 1.6-mm-diameter-wire. Experiments covered the range between 300 and 1900 K; thermometry was provided by Pt10%Rh/Pt and W5%Re/W25%Re thermocouples. The maximum uncertainties in the specific heat capacity and electrical resistivity determinations were less than 3 and 1%, respectively. Results are reported and discussed for both the bcc and hcp structures and the transformation between the two phases.

KEY WORDS: electrical conductors; electrical resistivity; high temperatures; specific heat capacity; titanium; solid–solid transformation metals.

1. INTRODUCTION

Published values of the specific heat capacity of α-titanium with an hcp structure are in fair agreement below room temperature. In the range from room temperature to the hcp–bcc transformation point, they are in less accord. The values for β-titanium with a bcc structure are in obvious discord, with respect to both the magnitude and the character of their temperature functions. Measurements presented in this paper were undertaken to contribute to a better understanding of the specific heat capacity and electrical resistivity of titanium in the complete range from ambient to near the melting temperature.

A variant of a millisecond-resolution pulse-heating method based on contact thermometry was applied, the heating to 1900 K taking about 1 s and the cooling to below 1000 K about 15 to 20 s. Because of the tendency

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of titanium to adsorb oxygen and nitrogen at elevated temperatures, it was necessary to reduce the duration of specimen surface exposure to elevated temperatures, which was largely met by the experimental conditions of the applied technique.

2. EXPERIMENTAL

The method, apparatus, experimental procedure, and discussion of measurement uncertainties have been presented previously [1]. Experiments were performed on seven specimens of titanium[3] wire with a nominal diameter of 1.6 mm. The length of the first specimen was 250 mm. The length of the second one was reduced to 200 mm to enable higher heating rates, while the next two had a 125-mm length. Three additional specimens with a length of 155 mm obtained at a later date provided data which supported the statistics of the experiments.

DC pulses lasting about 1 s were delivered by two heavy-duty 12-V batteries connected in series, resulting in heating rates of 800 to 1700 $K \cdot s^{-1}$. The specimen temperatures based on the International Temperature Scale of 1990 were measured using 0.05-mm-diameter PtRh10%/Pt or 0.1-mm-diameter W5%Re/W25%Re thermocouples. The specific heat capacity and electrical resistivity were computed following the procedure described in Ref. 1. The experiments were performed on specimens as received, without additional thermal treatment.

3. RESULTS

The electrical resistivity and specific heat capacity were measured in 30 experiments. Eighteen of them were limited to the hcp range, and 12 extended into the bcc range. Seven of them reached a few degrees below the melting point.

Experiments in the hcp range are represented by smooth interpolated functions: electrical resistivity ($\Omega \cdot m$), valid in the range 300 to 1152 K,

$$R_o = -2.943 \times 10^{-7} + 2.559x10^{-9}T - 3.602 \times 10^{-13}T^2 - 3.280 \times 10^{-16}T^3 \quad (1)$$

and specific heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$), valid between 360 and 1106 K,

$$C_p = 405.6 + 5.0757 \times 10^{-1}T - 2.781 \times 10^{-4}T^2 + 8.750 \times 10^{-8}T^3 \quad (2)$$

[3] The specimens were provided courtesy of the late Dr. Ared Cezairlyan, NIST.

In the bcc range, smooth interpolated functions of the electrical resistivity and specific heat capacity are given by

$$R_o = 1.170 \times 10^{-6} + 4.215 \times 10^{-10} T - 1.374 \times 10^{-13} T^2 + 2.536 \times 10^{-17} T^3 \tag{3}$$

valid in the range 1168 to 1930 K, and

$$C_p = -1689.3 + 5.230T - 3.920 \times 10^{-3} T^2 + 9.826 \times 10^{-7} T^3 \tag{4}$$

valid between 1202 and 1910 K.

Deviations of electrical resistivities obtained in individual experiments from the final function Eq. (1) were from $\pm 1.5\%$ at 370 K to $\pm 1.7\%$ at 1070 K. In the bcc range, deviations from the function Eq. (3) did not exceed $\pm 1\%$.

Corresponding deviations of individual specific heat capacities from the function Eq. (2) were from $\pm 1.1\%$ at 370 K to $\pm 2.2\%$ at 1070 K and from function Eq. (4) in the bcc range within $\pm 2.3\%$ limits.

3.1. Electrical Resistivity

Interpolated electrical resistivity functions Eqs. (1) and (3) are shown in Fig. 1 as continuous curves. The range of phase transformation from an

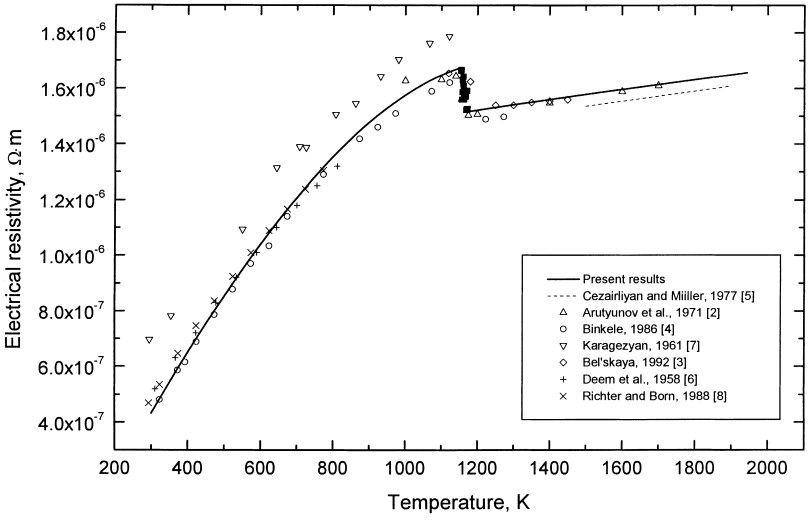

Fig. 1. Electrical resistivity as a function of temperature.

hcp to a bcc structure is interpreted with few averaged data points (filled squares). Figure 1 also contains data of Arutyunov et al. [2], Bel'skaya [3], Binkele [4], Cezairliyan and Miiller [5], Deem et al. [6], Karagezyan [7], and Richter [8].

Results of Deem et al. [6] and Richter [8] are limited to the range between room temperature and about 800 K, and those of Karagezyan [7] extend from the same lower temperature to below the hcp–bcc transformation. Results of Bel'skaya [3] start just below the transformation and extend to 1450 K, and results of Arutyunov et al. [2] cover the range from 1000 to 1400 K. Results of Cezairliyan and Miiller [5] are confined to the bcc range between 1500 and 1900 K. Present results and those of Binkele [4] extend from room temperature into the bcc range.

In the present study, the room-temperature electrical resistivity was also measured with the aid of the stationary state four-probe current reversal method. Measurements were carried out on one specimen before and after the end of the pulse experiments. The effect of six pulse measurements was a slight decrease in the room-temperature electrical resistivity, amounting to 0.6%, indicating that titanium was not originally in an annealed state.

Electrical resistivity values reported in this research have not been corrected for thermal expansion.

3.2. Specific Heat Capacity

Figure 2 contains specific heat capacity functions, Eqs. (2) and (4). Discrete values (filled squares) in the range between them indicate a change of specific heat at the phase transition. Figure 2 also shows low-temperature values of Kothen and Johnston [9], the values above room temperature of Arutyunov et al. [2], Bendick and Pepperhoff [10], Kohlhaas et al. [11], Kothen [12], and Peletski et al [13], and the high-temperature values of Cezairliyan and Miiller [5]. The function of Hultgren et al. [14], based on results of Kothen and Johnston [9], Kelley [15], Yaeger et al. [16], and some other authors, is not shown, since, in the hcp range, it follows values of Kothen [12], and in the bcc range, it is in close agreement with more recent values of Kohlhaas et al. [11].

The low-temperature specific heat capacity of titanium is represented in Fig. 2 only by values of Kothen and Johnston [9] above 160 K, although they originally extend from 15.4 to 305.5 K. The values of Kelley [15] are not shown, as they are in perfect agreement with the former.

The present results at their lowest temperature (370 K) join smoothly onto those of Kothen and Johnston [9], agreeing up to 900 K with the values of Kohlhaas et al. (320 to 1800 K) [11] and Bendick and Pepperhoff

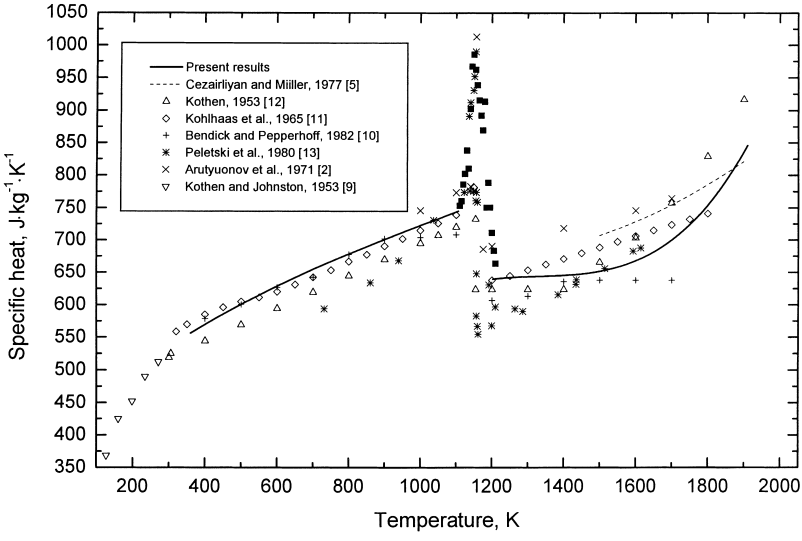

Fig. 2. Specific heat capacity as a function of temperature.

(400 to 1700 K) [10] within ±0.5%. Above this temperature, the latter start to lag below the other two, the maximum deviation being 5% at about 1150 K. Specific heat capacity values quoted by Peletski et al. (730 to 1600 K) [13] start about 5% below the band formed by the above three data sets at 731 K, to join and supersede them at 1000 K. Values of Arutyunov et al. (1000 to 1700 K) [2] start about 4% above this band at 1000 K, to join the general trend before the transformation peak. Values of both Peletski et al. [13] and Arutyunov et al. [2] approach the transformation peak with a steeper trend with changing temperature.

In the bcc range below 1900 K, scatter of the literature values ranges from 11.5% at 1200 K to 12.5% at the upper limit. Trends of the different data sets differ markedly. While some of them follow basically a linear law (Bendick and Pepperhoff [10] and Kohlhaas et al. [11]), where the first is virtually independent of temperature and the second has a stable rising trend with increasing temperature, other values show a combination of the two. The values of Kothen [12] and the results of the present work are temperature independent at the beginning but increase steeply as the melting point is approached. The only difference between them is in the onset of this increase. Kothen [12] observed this at about 1450 K, while in the present measurements, the onset is shifted to a temperature about 100 K higher.

In the range of about 50 K on either side of the hcp–bcc transformation, values of all authors virtually coincide, which is true particularly for the rising portion. Certain differences appear in the falling portion, where results of Kothen [12] and Peletski et al. [13] indicate a faster return from the transformation.

The present electrical resistivity measurements have defined the position of the transformation temperature at 1164 ± 1 K, while the specific heat capacity results gave 1160 ± 1 K. On the basis of electrical resistivity measurements, Bel'skaya [3] reported the transformation between 1150 and 1160 K. Cezairliyan and Miiller [5] reported a value of 1165 K. Hultgren et al. [14] defined the transformation at 1155 K, and McQuillan and McQuillan [17], based on measurements of resistivity and hydrogen pressure, thermoelectric force, and thermal arrest, as well as thermodynamic calculations, located it between 1155 and 1161 K.

3.3. Measurement Uncertainties

Estimation of maximum uncertainties in the specific heat capacity and electrical resistivity measurements by this method is given by Dobrosavljević and Maglić [1], who define them at 3 and 1%, respectively. Uncertainties typically reach their maximum values close to the upper and lower limits of the measurement range.

4. DISCUSSION

4.1. Electrical Resistivity

All electrical resistivity results presented in Fig. 1 follow the same general pattern. With the exception of the Karagezyan data [7], they are all confined within a band of about $\pm 12.5\%$ at room temperature and $\pm 2.5\%$ below the transformation. The values of Karagezyan [7] lie about 40% above this band at 300 K and about 9% at 1100 K. At the beginning of the measurement range, the present values are in good agreement with those of Binkele [4], but exceed them at 1000 K by about 2.5%. In the bcc range they agree with the values of Arutyunov et al. [2] and Bel'skaya [3]. The values of Binkele [4] and the values of Cezairliyan and Miiller [5] lie about 2% lower.

The difference of 2% is within the measurement uncertainty of the reported values of the different authors. Moreover, two data points of Binkele [4] in the bcc range are close to the end of his measurements,

extending in this phase only for 100 K. Measurements of Cezairliyan and Miiller [5] cover only 400 K, near the lower margin of their high-temperature pulse calorimetry facility.

The observed disagreement between the electrical resistivity values of Karagezyan [7] and other values in the hcp range might be related to the chemical composition of his specimen, which was designated "industrial purity."

4.2. Specific Heat Capacity

Agreement among the results of a number of authors, from low temperatures throughout the hcp range is sufficiently good. Above room temperature, agreement is particularly good among the results of Kohlhaas et al. [11], Bendick and Pepperhoff [10], and the present work. They are supported by values of Kothen [12] having the same character, positioned some 4 to 5% lower.

As mentioned before, disagreement is most pronounced in the bcc range. Cezairliyan and Miiller [5] rightfully ascribe the character of a number of results to the techniques used in the measurements. The drop technique, when applied in a relatively narrow temperature range with a limited number of measured enthalpies, is likely to give specific heat functions heavily dependent on the type of polynomial selected for their fitting. Frequently a linear function or even a constant value, independent of temperature, is used (Yaeger et al. [16], Golutvin [18], Serebryannikov and Gel'd [19], Berezin et al. [20]). The modulation technique would be expected to give more adequate results. However, the frequently cited measurements of Holland [21] involved too many innovations on the experimental side, resulting in excessive scatter of the obtained values. Results of Arutyunov et al. [2] are much more interesting. The same applies to adiabatic calorimetry applied by Kohlhaas et al. [11] and Bendick and Pepperhoff [10]. Adiabatic calorimetry at high temperatures becomes very sensitive to errors due to radiation heat exchange. The millisecond-resolution pulse calorimetry used in the present work and its high-temperature variant applied by Cezairliyan and Miiller [5] seem more appropriate for a metal as reactive as titanium. Exposing specimens to high temperatures for only a few tens of seconds may offer many advantages.

A variant of the pulse technique using a capacitor bank discharge applied by Parker [22], with heating rates between 10^4 and $10^9\,\mathrm{K}\cdot\mathrm{s}^{-1}$, enabled estimation of the time needed for hcp–bcc transformation.

To keep Fig. 2 readable, results of Yaeger et al. [16], Golutvin [18], Serebryannikov and Gel'd [19], Berezin et al. [20], Holland [21], and Parker [22] are not shown.

The increase in the specific heat capacity with increasing temperature observed by Kothen [12], Holland [21], and Kohlhaas et al. [11] and in the present work is interesting. When Hultgren et al. [14] were preparing their *Selected Values of Thermodynamic Properties of Metals and Alloys*, only the values of Kothen [12] were available. They disregarded the values of Kothen [12] above 1700 K, supposing that they were characterized by premelting of impurities. Since then, this phenomenon was reported in measurements using different techniques: modulation technique by Holland [21], adiabatic calorimetry by Kohlhaas et al. [11], and the millisecond-resolution pulse technique, employed in the present study. All present experiments exceeding 1500 K confirmed such dependence. The same shape of the specific heat capacity function in the high-temperature range was observed with zirconium, another metal from Group IVa (Maglić et al. [23]). Kraftmakher might rightfully ascribe this phenomenon to vacancy formation [24].

Finally, difficulties in experiments due to elongation of specimens and disengagement of thermocouple wires at high temperatures should be mentioned. Of course, measurements in which specimens changed their diameter after experiments were disregarded, and the specimen in question was not used further. Disengagement of thermocouple wires, which occurred frequently in the transition from the hcp to the bcc range, required repetition of experiments.

ACKNOWLEDGMENTS

The research reported in this paper was funded by the Serbian Ministry for Science and Technology. The Authors acknowledge with thanks the contribution of the late Dr. Ared Cezairliyan of the National Institute of Standards and Technology, Gaithersburg, Maryland, for providing titanium specimens for this study. The THERSYST thermophysical properties data bank for solid materials, developed and operated by the University of Stuttgart-IKE, provided valuable literature data on electrical and calorimetric properties of titanium, which contributed significantly to the completeness of this study and are gratefully appreciated.

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