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Enthalpy and Temperature of the Titanium Alpha-Beta Phase Transformation[1]

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The specific enthalpy and the temperature of the titanium α-β phase transformation were measured by a pulse-heating system operating in the millisecond time regime. The measurement technique is based on self-heating of a tube-shaped specimen from room temperature to the beta phase of titanium. A comparison between the measured phase transition temperature during heating and cooling of the specimen shows a difference of approximately 20 K. The temperature measured during the heating period is higher than the value obtained from the cooling cycle of the specimen. For the evaluation of the specific enthalpy of the alpha-beta transformation, the specific enthalpy versus temperature function of the beta phase of the heating period was extrapolated to the transition temperature obtained from the cooling cycle (1152 K). A total of 12 measurements on 3 tube-shaped specimens was made, an average value of 89.9 $\mathrm{kJ \cdot kg^{-1}}$ was obtained for the specific enthalpy of the transformation. The reproducibility of the measured specific enthalpy at the beginning and at the end of the transformation was 0.5%. The reproducibility of the phase transformation enthalpy as difference between the beginning and the end was 3%. The extended measurement uncertainty (at a confidence level of 95%) is estimated to be $\pm 6\%$ for the specific enthalpy of the transformation and ± 6 K for the transformation temperature.

KEY WORDS: high temperature; solid–solid phase transformation; titanium; transformation enthalpy, transformation temperature.

1. INTRODUCTION

The α-β phase transformation of titanium has been investigated by several groups using different methods. Unfortunately, the values presented in the

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literature for the transition temperature and enthalpy vary considerably. This may be expected in view of the reactive nature of titanium as well as problems with heat losses due to thermal radiation and heat conduction to the environment.

The method used to measure enthalpy and transformation temperature is based on rapid resistive self-heating of a tubular specimen from room temperature to high temperature in a short time by passage of a high electrical current through the specimen. Simultaneously, the specimen temperature, current through the specimen, and voltage drop across a defined portion of the specimen are measured time-resolved. Subsecond techniques eliminate any significant contact between specimen and surroundings. Due to the short duration of these experiments, the heat losses due to radiation are minimal.

2. EXPERIMENTAL

A description of the construction and operation of the pulse-heating system and the single-wavelength high-speed pyrometer is given in Refs. 1 and 2. The specimen is electrically pulse-heated from room temperature to a pre-chosen temperature in less than 300 ms. The specimen temperature is measured by a fast single-wavelength pyrometer every 0.5 ms. The effective wavelength of the interference filter of the pyrometer is 902 nm with a bandwidth (FWHM) of 20 nm. The pyrometer has been calibrated by means of a vacuum tungsten strip lamp covering a temperature range of 1000 to 1700 K. Reported temperatures are based on the International Temperature Scale of 1990 (ITS-90) [3].

The heated specimen is a tube with a length of approximately 75 mm, an outer diameter of 10.2 mm, and an inner diameter of 8.6 mm. To approximate blackbody conditions for the temperature measurement, a rectangular hole of 0.5×1.6 mm is machined into the wall of the specimen. Material is removed on the remaining length to achieve a constant cross section over the full length.

3. MEASUREMENTS

On the basis of typical analyses by the manufacturer, Goodfellow Metals, Cambridge, United Kingdom, the specimen material is reported to be 99.6% pure, containing the following impurities (in ppm per mass): O, 2000; Fe, 1500; Al, Si, C, 300 each; Sn, 200; N, 150; Mn 100; H 60; Cr, Ni, 50 each; Ca, 20; Cu, 5. A total of 12 measurements was made on three tubular specimens in the temperature range from 1100 to 1250 K. All experiments were performed either in an argon environment or under high-vacuum conditions to prevent problems associated with chemical reactions. The initial temperature of the specimen was 298 K.

An example of the measured temperature of the specimen during heating and subsequent cooling is shown in Fig. 1. The specific enthalpy h as a function of time t was calculated from data obtained during the heating period in the millisecond range. A small correction for power loss due to thermal radiation on the order of 0.5% has been made assuming a total hemispherical emissivity $\varepsilon_{\mathrm{tot}} = 0.3$,

$$h(t) = \int_0^t \left\{ \frac{U(t)\, I(t)}{m_{\mathrm{eff}}} - \sigma \varepsilon_{\mathrm{tot}} A \left[T(t)^4 - T_{\mathrm{a}}^4 \right] \right\} \mathrm{d}t \tag{1}$$

where U is voltage, I is current, m_{eff} is effective mass, σ is the Stefan-Boltzmann constant, A is the area of the radiating surface of the specimen, T is the specimen temperature, and T_{a} is the ambient temperature.

Eliminating the time dependence, the specific enthalpy can be plotted as a function of temperature (Fig. 2). For the evaluation, polynomials have been fitted to the specific enthalpy data of α-titanium, $h_{\alpha}(T)$ and β-titanium, $h_{\beta}(T)$ by the least-squares method. The transformation temperature $T_{\alpha\text{-}\beta}$ was obtained from the temperature plateau during the cooling phase (Fig. 1). The transformation enthalpy $h_{\alpha\text{-}\beta}$ is the difference between the

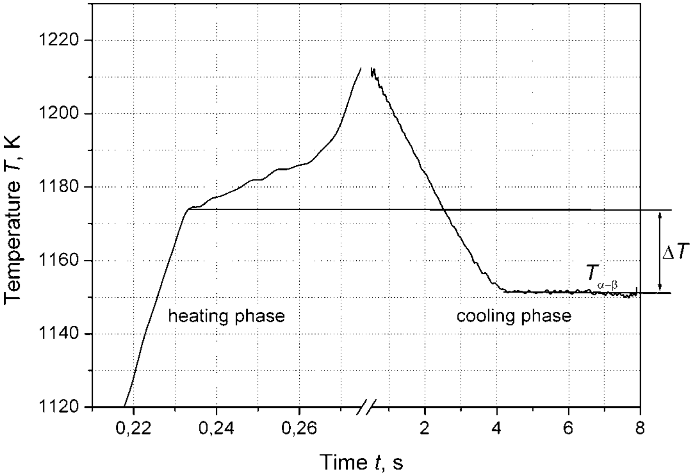

Fig. 1. Specimen temperature T as a function of time t as measured in a typical experiment during heating and cooling. $T_{\alpha\text{-}\beta}$ is the transformation temperature obtained from the cooling phase.

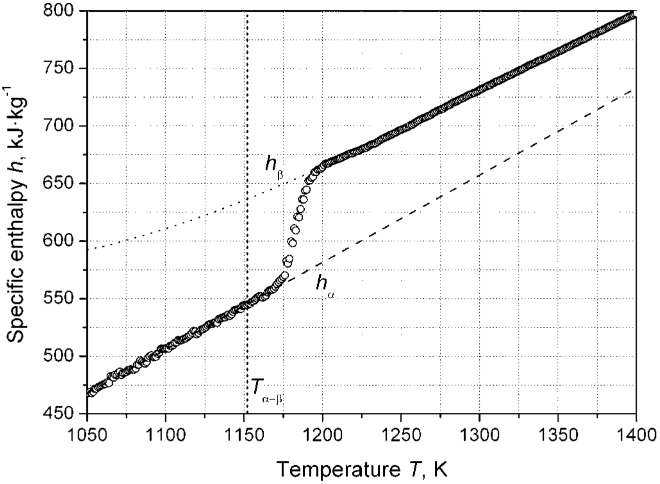

Fig. 2. Specific enthalpy h of titanium as a function of temperature T. Circles, measured data; dashed line, specific enthalpy of the α-phase; dotted line, specific enthalpy of the β-phase; short dashed line, transformation temperature obtained during the cooling phase.

specific enthalpy in the α-phase and the β-phase at the transformation temperature $T_{\alpha\text{-}\beta}$:

$$h_{\alpha\text{-}\beta} = h_{\beta}(T_{\alpha\text{-}\beta}) - h_{\alpha}(T_{\alpha\text{-}\beta}). \tag{2}$$

4. RESULTS

The transformation temperatures $T_{\alpha\rightarrow\beta}$ of 12 measurements on three different specimens have been averaged, resulting in a value of the transformation temperature of $T_{\alpha\rightarrow\beta} = 1152$ K. The transformation temperature was obtained from the cooling phase of the experiment. The transformation temperature during the heating phase is, depending on the heating rate, about 20 K higher (Fig. 1) and does not seem to represent thermal equilibrium conditions. The average transformation enthalpy is $h_{\alpha\rightarrow\beta} = 89.9\ \mathrm{kJ\cdot kg^{-1}}$.

5. ESTIMATE OF UNCERTAINTIES

An analysis of uncertainties for the transformation enthalpy is given in Table I and is calculated as recommended in Ref. 4. The uncertainty of the specific enthalpy of the transformation is estimated to be less than $\pm 6\%$.

Table I. Estimation of the Uncertainty of the α-β Phase Transformation Enthalpy of Titanium

Source of Uncertainty		Value	Standard uncertainty	Sensitivity coefficient	Contribution to total uncertainty
Current	Voltage measurement	0.7578 V	0.0017 V	$119\ \mathrm{kJ \cdot kg^{-1} \cdot V^{-1}}$	$0.202\ \mathrm{kJ \cdot kg^{-1}}$
	Instrumentation amplifier, gain	10.000	0.005	$9.00\ \mathrm{kJ \cdot kg^{-1}}$	$0.045\ \mathrm{kJ \cdot kg^{-1}}$
	Shunt resistor	40.0 μΩ	0.2 μΩ	$2.25\ \mathrm{kJ \cdot kg^{-1} \cdot \mu\Omega^{-1}}$	$0.450\ \mathrm{kJ \cdot kg^{-1}}$
Voltage	Voltage divider	2.000	0.004	$45.0\ \mathrm{kJ \cdot kg^{-1}}$	$0.180\ \mathrm{kJ \cdot kg^{-1}}$
	Voltage measurement	2.4601 V	0.0029 V	$36.5\ \mathrm{kJ \cdot kg^{-1} \cdot V^{-1}}$	$0.106\ \mathrm{kJ \cdot kg^{-1}}$
Specimen	Total length	75.11 mm	0.02 mm	$1.20\ \mathrm{kJ \cdot kg^{-1} \cdot mm^{-1}}$	$0.024\ \mathrm{kJ \cdot kg^{-1}}$
	Effective length	34.69 mm	0.05 mm	$2.59\ \mathrm{kJ \cdot kg^{-1} \cdot mm^{-1}}$	$0.130\ \mathrm{kJ \cdot kg^{-1}}$
	Total mass	7.4388 g	0.0010 g	$12.1\ \mathrm{kJ \cdot kg^{-1} \cdot g^{-1}}$	$0.012\ \mathrm{kJ \cdot kg^{-1}}$
Pyrometer	Temperature	1152.0 K	3.0 K	$0.078\ \mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$	$0.234\ \mathrm{kJ \cdot kg^{-1}}$
Evaluation	Extrapolation of h_β	$0.0\ \mathrm{kJ \cdot kg^{-1}}$	$2.6\ \mathrm{kJ \cdot kg^{-1}}$	1.00	$2.600\ \mathrm{kJ \cdot kg^{-1}}$
Total uncertainty					$2.668\ \mathrm{kJ \cdot kg^{-1}}$
Expanded total uncertainty					$5.337\ \mathrm{kJ \cdot kg^{-1}}$

The uncertainty of the transformation temperature is estimated to be less than ±6 K. A detailed analysis of uncertainties for the temperature measurement is given in Ref. 2. The reported uncertainties are based on the standard uncertainty multiplied by a coverage factor of 2, providing a level of confidence of approximately 95%.

6. DISCUSSION

The temperature of the α-β phase transformation of titanium seems to depend on the heating rate. At high heating rates (about 3800 $K \cdot s^{-1}$), the transformation temperature is shifted to a higher temperature in comparison with the phase transformation temperature obtained from the cooling phase (Fig. 1). It should be noted that the temperature is not constant during the phase transformation, which also seems to be an effect of the high heating rate. There should be awareness that rapid heating produces a significant shift in the solid–solid transformation temperature, since the material is not in an equilibrium state. Therefore the transformation temperature has been measured during the cooling phase with its low cooling rate.

Cezairliyan and Miiller [5] used a very similar method to measure the transformation enthalpy, the transformation temperature, and the electrical resistivity of α-titanium and β-titanium in the vicinity of the phase transformation. The transformation energy of titanium reported in this paper is 4170 $J \cdot mol^{-1}$, which is equivalent to 87.1 $kJ \cdot kg^{-1}$, assuming an atomic weight of 47.867 $g \cdot mol^{-1}$ [6], and is approximately 3% lower than our value. The transformation temperature given in [5] is 1166 K on IPTS-68. This value is 14 K higher than the result of this work, but the transformation temperature has been obtained from the heating phase with a high heating rate.

Martynyuk et al. [7] used a very rapid pulse heating system providing heating rates in the range of 4×10^6 to 10^7 $K \cdot s^{-1}$ to investigate titanium with a nominal purity of 99.74%. The transformation enthalpy reported in [7] is 4300 $J \cdot mol^{-1}$ which is equivalent to 89.8 $kJ \cdot kg^{-1}$. Kohlhaas et al. [8] used titanium with a purity of 99.8% for his measurements. The transformation enthalpy obtained in [8] is 4150 $J \cdot mol^{-1}$ which is equivalent to 89.7 $kJ \cdot kg^{-1}$; the transformation temperature is 1167 K on IPTS-48.

An exhaustive compilation of older work done on the thermodynamic properties of titanium is given in Ref. 9. It recommends the values of transition enthalpy and transition temperature of Cezairliyan and Miiller [5]. This does not take into account the problem of nonequilibrium conditions when titanium is heated so rapidly. In our opinion, the equilibrium temperature value of the alpha-beta phase transition is several degrees lower than this recommendation.

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