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Thermodynamic Studies of the $\alpha \rightarrow \beta$ Phase Transformation in Zirconium Using a Subsecond Pulse Heating Technique*

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Measurements of the temperature and energy of the $\alpha \rightarrow \beta$ phase transformation, and the electrical resistivity near and at the transformation point of zirconium using a subsecond duration pulse heating technique are described. The results yield 1147 K for the transformation temperature and 3980 $J \cdot mol^{-1}$ for the transformation energy. Electrical resistivity is found to decrease by 17 percent during the transformation. Estimated inaccuracies of the measured properties are: 10 K for the transformation temperature, 5 percent for the transformation energy, and 2 percent for the electrical resistivity.

Key words: Electrical resistivity; high-speed measurements; high temperature; solid-solid phase transformation; thermodynamics; zirconium.

1. Introduction

In another publication [1],[1] the applicability of a rapid pulse heating technique to studies of solid-solid phase transformations at high temperatures was demonstrated by measurements on iron at the $\gamma \rightarrow \delta$ transformation point.

The objective of the work described in this paper has been to apply the same technique to studies of the $\alpha \rightarrow \beta$ phase transformation in zirconium. Measurements of the temperature and energy of the phase transformation, and electrical resistivity near and at the transformation point are reported.

The method is based on rapid resistive self-heating of the specimen from room temperature to high temperatures in less than one second by the passage of an electrical current pulse through it; and on measuring, such experimental quantities as current through the specimen, potential drop across the specimen, and specimen temperature. Recordings of the experimental quantities are made digitally every 0.4 ms with a full-scale signal resolution of approximately one part in 8000. Specimen temperature is measured with a high-speed photoelectric pyrometer [2]. The details regarding the construction and operation of the measurement system are given in earlier publications [3, 4].

2. Measurements

The measurements were made on three zirconium specimens of 99.98% purity. The specimens were tubes fabricated from rods by removing the center portion using an electro-erosion technique. The nominal dimensions of the specimens were: length, 76.2 mm; outside diameter, 6.3 mm; and wall thickness, 0.5 mm. The outer surfaces of the specimens were polished to reduce heat loss due to thermal radiation. According to the manufacturer's analysis, the specimens contained the following impurities, in ppm by weight: O, 125; Hf, 40; Fe, 30; C, 6; H, 3.3; Al, 3; N, 2.1; Ni and Si, 1.5 each; and Ti, 1. The total amount of all other detected elements was less than 6 ppm, each element being below 1 ppm limit.

Duration of the current pulses ranged from 220 to 620 ms. Specimen heating rates varied from 1800 $K \cdot s^{-1}$ to 4000 $K \cdot s^{-1}$. All the experiments were conducted with the specimens in a vacuum environment of approximately 1.3×10^{-3} $N \cdot m^{-2}$ ($\sim 10^{-5}$ torr).

The $\alpha \rightarrow \beta$ transformation (from hexagonal close-packed form to body-centered cubic) was manifested by a plateau in the temperature versus time relation for the specimen during heating. The transformation temperature for each specimen was obtained by averaging the temperatures at the plateau.

The transformation energy was obtained from the time integral of the power absorbed by the specimen during the transformation as defined by the plateau. The instantaneous value of the absorbed power was obtained by subtracting the calculated power loss due

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[1] Figures in brackets indicate the literature references at the end of this paper.

to thermal radiation from the imparted power (current through the specimen times the potential drop across the specimen). The hemispherical total emittance needed for this computation was obtained from the extrapolation of the measurements above 1500 K reported in an earlier publication [5]. Since the calculated power loss from the specimen due to thermal radiation was not greater than 1 percent of power imparted at the transformation temperature, even a considerable uncertainty (10%) in the emittance does not contribute any significant errors to the absorbed power.

3. Experimental Results

Except where explicitly noted, all temperatures reported in this paper are based on the International Practical Temperature Scale of 1968 [6]. In all computations, the geometrical quantities are based on their room temperature (298 K) dimensions. The experimental results for the temperature and energy of the $\alpha \rightarrow \beta$ phase transformation are presented in table 1.

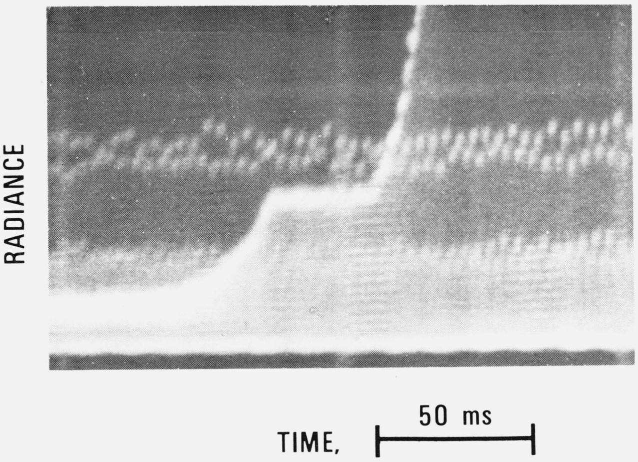

FIGURE 1. *Oscilloscope trace photograph of specimen radiance near and at the transformation point of zirconium as measured with the high-speed pyrometer.*

Dots forming the long horizontal lines correspond to radiances from a reference source.

TABLE 1. *Results for the $\alpha \rightarrow \beta$ transformation temperature and transformation energy of zirconium*

Specimen number	Heating rate [a] ($K \cdot s^{-1}$)	Number of temperatures [b]	Transformation temperature (K)	Standard deviation [c] (K)	Transformation energy ($J \cdot mol^{-1}$)
1	4000	27	1144.9	3.4	3993
2	1800	61	1148.4	3.2	3970
3	3100	47	1146.6	3.4	3968

[a] Evaluated approximately 50 K below the transformation point.

[b] Number of temperatures at the plateau used to obtain the average transformation temperature for a specimen.

[c] Standard deviation of an individual temperature at the plateau from the average transformation temperature for a specimen.

The average value of the transformation temperatures of the three specimens is 1146.6 K with a maximum and average difference of individual specimens from this value of 1.8 K and 1.2 K, respectively. The average value for the transformation energy is 3977 $J \cdot mol^{-1}$ with a maximum and average absolute difference from this value of 0.4 percent and 0.3 percent, respectively. It may be concluded that for $\alpha \rightarrow \beta$ transformation in zirconium, the transformation temperature is 1147 K and the transformation energy is 3980 $J \cdot mol^{-1}$.

As discussed in an earlier publication [5], the measurements of the geometrical quantities of a zirconium specimen after a number of experiments indicated permanent distortions (elongation) due to repeated heating and cooling through the transformation point. The values reported in this paper correspond to the first experiment for a specimen, for which no correction was needed.

Typical experimental results are presented in figures 1, 2, 3, and 4, all referring to specimen 3. Specimen radiance and specimen temperature near and at the transformation point are shown in figures 1 and 2, respectively. Figure 3 shows the variation of electrical resistivity as a function of time, while the variation of resistivity with temperature is shown in

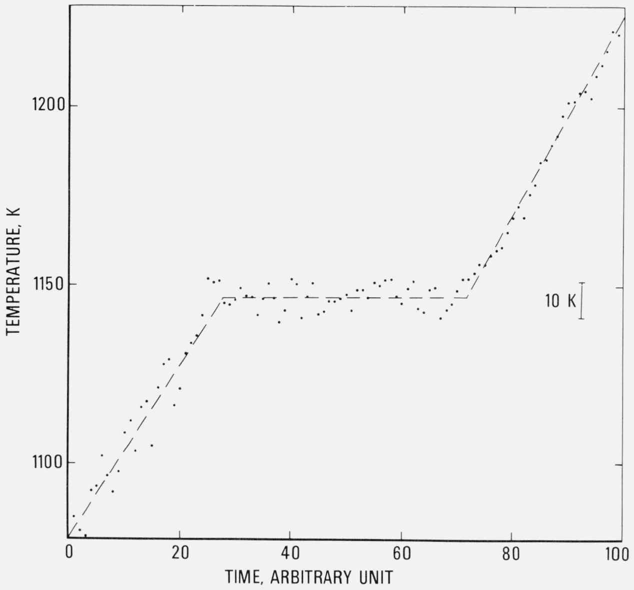

FIGURE 2. *Variation of temperature as a function of time near and at the transformation point of zirconium. The points are the temperatures obtained from individual pyrometer readings.*

The dashed lines represent the linear fits (obtained using the least-squares method) of the data in the three regions (below, during, and above the transformation). (1 time unit = 0.833 ms.)

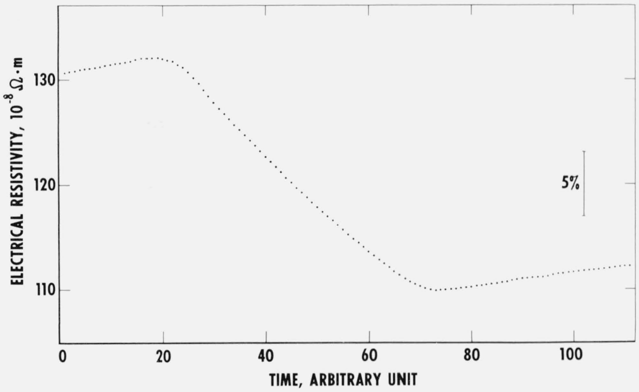

FIGURE 3. *Variation of electrical resistivity as a function of time near and at the transformation point of zirconium. The points are the resistivities obtained from individual data on current and voltage.*

(1 time unit = 0.833 ms.)

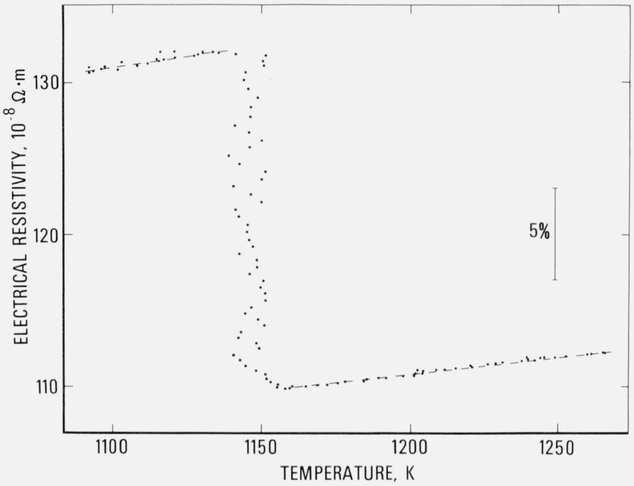

FIGURE 4. *Variation of electrical resistivity as a function of temperature near and at the transformation point of zirconium. The points are resistivities obtained from individual data on current and voltage.*

The two dashed lines represent the linear fits (obtained using the least-squares method) of the data below and above the transformation.

figure 4. It may be seen that the change in the electrical resistivity during the transformation was about 17 percent. Extrapolation of the resistivity values above the transformation to 1500 K is in agreement, within 0.3 percent, with those reported in an earlier publication [5].

The details of methods for estimating errors in measured and computed quantities using the present measurement system are given in an earlier publication [4]. In this paper the specific items were recomputed whenever the present conditions differed from those in the earlier publication.

The results obtained for imprecision [2] and inaccuracy [3] respectively are: 3 and 10 K for the transformation temperature, 1 and 5 percent for the transformation energy, and 0.5 and 2 percent for the electrical resistivity.

In the case of temperature, the standard deviation of an individual point from the average transformation temperature in a given experiment is approximately 3 K. For the three experiments, the average absolute difference of transformation temperatures from their mean is 1.2 K. In the case of energy, the imprecision includes the uncertainty in the computation of the time duration of the transformation plateau.

4. Discussion

The first evidence of a possible solid-solid phase transformation in zirconium was presented by Zwikker in 1926 [7]. Since his experiments were performed on zirconium heated in air, the transformation occurred over an extended temperature range. A sharp transformation was reported by Vogel and Tonn [8] from dilatometric and metallographic measurements and was confirmed by de Boer et al. [9], who noted that the temperature range was extended by small amounts of oxygen and nitrogen in the zirconium. The values for the $\alpha \rightarrow \beta$ transformation temperature for zirconium reported in the literature are given in table 2. Some of the old results could not be corrected to IPTS–68, due to insufficient information in the original papers. However, the contribution of the possible differences in the temperature scales may not exceed a few degrees at the transformation temperature.

TABLE 2. *Values of the $\alpha \rightarrow \beta$ transformation temperature of zirconium reported in the literature*

Investigator	Reference	Year	Temperature [a] (K)
Vogel and Tonn	8	1931	1135 ± 5
de Boer et al.	9	1936	1138 ± 10
Duwez	10	1951	1123 to 1138
Domagala and McPherson	11	1954	1135
Kneip and Betterton	12	1956	1138 to 1146
Vollmer et al.	13	1967	1155
Present work			1147 ± 10

[a] All temperatures in this table are those reported by the authors of the original papers. No correction to IPTS–68 was possible, due to insufficient information in the original papers.

The present value for the transformation temperature is higher than most of the values given in the literature. This may partly be due to the high heating rates used in this work. A similar effect, though in the opposite direction, was observed by Duwez [10] in experiments on rapid quenching of zirconium specimens (cooling rates from 4 to 10,000 $K\cdot s^{-1}$). The transformation

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[2] Imprecision refers to the standard deviation of an individual point as computed from the difference between measured value and either the average or the smooth function obtained by the least-squares method.

[3] Inaccuracy refers to the estimated total error (random and systematic).

TABLE 3. *Change of the electrical resistivity of zirconium during the α→ β transformation reported in the literature*

Investigator	Reference	Year	Temperature [a] of maximum resistivity (K)	Temperature [a] of minimum resistivity (K)	Ratio, $\frac{\rho_{max}}{\rho_{min}}$
Zwikker	7	1926	1150	1430	1.14
de Boer et al.	9	1936	1130	1145	1.19
Squire and Kaufman	17	1941	1067	1142	1.12
Adenstedt	18	1952	1118	1143	1.20
Rogers and Atkins	19	1955	1127	1173	1.19
Powell and Tye	20	1961	1129	1177	1.18
Present work			1134	1158	1.20

[a] All values in this table are based on the results reported by the authors of the original papers. No correction of values to IPTS–68 was possible, due to insufficient information in the original papers.

temperature was found to decrease with increasing cooling rate by as much as 15 K. This behavior was confirmed by Hayes and Kaufman [15]. The result of the energy of transformation of zirconium obtained in this work (3980 $J \cdot mol^{-1}$) is 6 percent higher than the value (3740 $J \cdot mol^{-1}$) of Douglas and Victor [14], 3 percent higher than the value (3850 $J \cdot mol^{-1}$) cf Coughlin and King [16], 0.1 percent higher than the most recent value (3975 $J \cdot mol^{-1}$) of Vollmer et al. [13], and 9 percent lower than the value (4350 $J \cdot mol^{-1}$) of Skinner [21].

The values 3980 $J \cdot mol^{-1}$ for the transformation energy and 1147 K for the transformation temperature yield a value of 3.47 $J \cdot mol^{-1} \cdot K^{-1}$ for the entropy of $\alpha \rightarrow \beta$ transformation in zirconium.

Because of the strong dependence of the electrical resistivity on composition for zirconium at the transformation point, it is difficult to compare resistivity values reported in the literature on an absolute basis. However, a meaningful comparison may be made based on the ratio of the maximum to the minimum resistivities for a given specimen. The results of such a comparison are given in table 3. High values for the ratio and small temperature range during which transformation is completed are indications of the high purity of the specimens.

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