

Calorimetric and Transport Properties of Zircalloy 2, Zircalloy 4, and Inconel 625

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This paper presents the measurements and the results on thermal and electrical transport properties of three nuclear reactor cladding materials: Zircalloy 2, Zircalloy 4, and Inconel 625. Study of these materials constituted a part of the IAEA coordinated research program aimed at the generation and establishment of a reliable and complete database of the thermal properties of reactor materials. Measured properties include thermal diffusivity, specific heat, and electrical resistivity. Thermal diffusivity was measured by the laser pulse technique. Specific heat and electrical resistivity were measured using a millisecond-resolution direct electrical pulse heating technique. Thermal conductivity was computed from the experimentally determined thermal diffusivity and specific heat functions and the room temperature density values. Measurements were performed in the 20 to 1500 C temperature range, depending on the material and property concerned.

KEY WORDS: electrical conductivity; nuclear fuel cladding; nuclear materials; thermal conductivity; thermal diffusivity; specific heat.

1. INTRODUCTION

Operational and safety assessments of nuclear reactors rely on models, computer programs, databases, and input parameters. Obviously, results obtained by the best computer programs can be only as good as the input data, of which the thermophysical properties of reactor materials constitute an important part. Thermophysical property data are needed for modeling the thermal behavior of materials under normal, transient, and accident conditions. The International Atomic Energy Agency (IAEA) analyzed the needs of its member states in this area, and a decision was made to

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organize a coordinated research program (CRP) aimed at the generation and establishment of a reliable and complete database for reactor materials.

The IAEA CRP for the establishment of a database for thermophysical properties of light-water and heavy-water reactor materials [1] includes study and evaluation of thermophysical properties of cladding materials: Zircalloy 2, Zircalloy 4, and Inconel 625. The CRP sets the lower-temperature limit of investigation at the ambient, with the upper tending to approach the material melting temperature. Investigation carried out at the Institute of Nuclear Sciences Vinča (NIV) as a participant of the CRP was limited to thermal diffusivity, specific heat, and electrical resistivity, the properties which could be measured with a good reliability and accuracy at its properties research laboratory. Results of this study are presented here.

2. EXPERIMENTAL PROCEDURES

2.1. Thermal Diffusivity Measurement

Thermal diffusivity was measured by the laser pulse method. The front face of a specimen (10 mm in diameter, between 1.7 and 3 mm in thickness) was exposed to a laser pulse, and the resulting rise in temperature at the rear face was detected optically. The measurement system was connected to a computer, for data acquisition and processing. This included filtering of the data and computation of thermal diffusivity values at given temperatures. A comparison of the experimental data with the temperature response predicted by the mathematical model indicated any departure of the experimental conditions from those assumed in the mathematical model and permitted the appropriate corrections to be introduced. The thermal diffusivity, a , was computed from

$$a = K_x \frac{L^2}{t_x} \quad (1)$$

where L is the specimen thickness, K_x is a constant corresponding to a percentage signal rise x , and t_x is the elapsed time between the initiation of the laser pulse and the rear surface temperature reaching percentage x of its maximum value. The use of a lead sulfide photoresistor for optical transient response detection limited contactless thermal diffusivity measurements to the range exceeding 250 °C. The maximum measurement uncertainty was estimated to be 3% [2].

2.2. Pulse Calorimetry

The specific heat and electrical resistivity of the specimens of the three investigated alloys in the shape of rods (3 to 4 mm in diameter and 200 mm

in length) were measured simultaneously, by a pulse heating method, with fast resistive heating of the specimen from room temperature to a predetermined maximum temperature [3]. Direct current pulses of 200–300 A allowed heating rates of 300–600 K · s⁻¹ to be achieved. Typically three thermocouples 0.05 mm in diameter of type K are welded intrinsically in the central zone of the specimen, at 10-mm separations. The central thermocouple is used to measure the specimen temperature. The other two monitor the temperature uniformity within the measurement zone, and their Chromel P legs are used as the potential leads for voltage drop measurements. The measurements are performed at 10⁻³ Pa. A computer system controls the experiment and is used for real-time data acquisition and subsequent processing. Data on the current, the voltage drop across the measurement zone, and the thermocouple emf are collected during specimen heating lasting 1500–2500 ms and for the duration of the initial cooling period. Several thousand data points are collected per run, yielding 500–1000 values of specific heat and electrical resistivity in the temperature range studied. The specific heat capacity, c_p , is computed from

$$c_p = \frac{(UI - P_r)}{m(d\theta/dt)} \quad (2)$$

and the electrical resistivity, ρ , is computed from

$$\rho = \frac{U}{I} \frac{S}{L_e} \quad (3)$$

where U is the voltage drop across the effective specimen length, L_e , between the potential leads, I is the current, P_r is the radiative power loss from the measurement zone, m is the mass of the effective specimen, $d\theta/dt$ is the heating rate at a given temperature, and S is the specimen cross section.

The maximum uncertainties in the specific heat capacity and electrical resistivity measurements are estimated to be 3 and 1%, respectively, except in the vicinity of anomalies, where they may reach larger values. An evaluation of errors is given in an earlier publication [3].

3. SPECIMENS

Zircalloy specimens were machined from 3- and 6-mm-thick Zircalloy sheets purchased from Sandvik (Sweden). The samples for thermal diffusivity measurement were 10 mm in diameter and 1.7 mm and 3.18 mm in thickness and were fabricated from respective plates. The first specimen for specific heat and electrical resistivity experiments, with a diameter of

Table I. Interpolated Experimental Values of Thermal Diffusivity, Specific Heat, and Electrical Resistivity, and Computed Values of Thermal Conductivity, for Zircalloy and Inconel 625 at Various Temperatures

Temperature, t (°C)	Thermal diffusivity, a ($10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$)		Specific heat, c_p ($\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$)		Electrical resistivity, ρ ($10^{-8} \Omega \cdot \text{m}$)		Thermal conductivity, λ ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	
	Zircalloy	Inconel 625	Zircalloy	Inconel 625	Zircalloy	Inconel 625	Zircalloy	Inconel 625
25	6.83	—	285.7	—	73.80	—	12.1	—
50	6.89	—	285.9	457.3	77.33	125.5	12.5	—
100	7.01	—	287.3	462.8	84.18	126.1	13.2	—
150	7.13	—	289.8	468.2	90.84	126.6	13.9	—
200	7.27	3.25	293.3	473.5	96.99	127.1	14.5	13.0
250	7.41	3.41	297.6	478.9	102.7	127.6	15.2	13.7
300	7.56	3.57	302.5	484.6	108.1	128.0	15.8	14.5
350	7.72	3.73	307.9	491.0	113.0	128.5	16.4	15.4
400	7.88	3.88	313.6	497.8	117.5	128.8	17.1	16.2
450	8.05	4.03	319.4	504.2	121.5	129.2	17.7	17.1
500	8.24	4.17	325.1	511.0	125.1	129.6	18.4	17.9
550	8.42	4.31	330.5	520.6	128.1	129.9	19.1	18.9
600	8.62	4.47	335.8	530.2	130.7	130.2	19.9	19.9
620	—	4.54	—	534.6	—	130.4	—	(20.3) ^u
640	—	4.62	—	546.1	—	130.5	—	(20.7)
650	8.83	—	341.3	—	132.8	—	20.7	—
660	—	4.71	—	586.9	—	130.5	—	(21.1)
680	—	4.78	—	644.2	—	130.2	—	(21.5)
700	9.04	4.84	347.3	702.0	134.5	129.7	21.5	(21.9)
720	—	4.73	—	664.4	—	129.2	—	(22.3)
740	—	4.60	—	638.3	—	128.8	—	(22.7)
750	9.26	—	354.3	—	135.8	—	22.5	—

760	--	4.54	--	626.2	--	128.5	--	(23.1)
780	--	4.55	--	620.3	--	128.3	--	(23.5)
800	9.49	4.59	360.7	618.6	136.9	128.1	(23.0)	23.9
820	9.58	--	361.5	--	137.2	--	(23.3)	--
840	9.68	--	361.8	--	137.5	--	(23.6)	--
850	--	4.71	--	621.1	--	127.8	--	24.6
860	10.1	--	384.0	--	137.7	--	(23.9)	--
880	10.7	--	493.1	--	137.3	--	(24.2)	--
900	11.2	4.84	611.0	626.9	135.7	127.6	(24.5)	25.5
920	11.7	--	677.4	--	133.6	--	(24.7)	--
940	12.1	--	716.4	--	130.9	--	(25.0)	--
950	--	4.97	--	634.4	--	127.4	--	26.5
960	12.4	--	746.2	--	127.6	--	(25.3)	--
980	12.7	--	790.5	--	124.1	--	(25.6)	--
1000	12.9	5.10	695.6	642.3	120.9	127.3	(25.9)	27.5
1020	--	--	522.4	--	119.2	--	--	--
1040	--	--	395.9	--	118.7	--	--	--
1050	--	5.20	--	--	--	--	--	--
1060	--	--	335.2	--	118.8	--	--	--
1080	--	--	329.7	--	119.1	--	--	--
1100	--	5.30	325.8	--	119.4	--	--	--
1150	--	--	322.2	--	120.4	--	--	--
1200	--	--	326.6	--	121.6	--	--	--
1250	--	--	337.7	--	122.7	--	--	--
1300	--	--	354.0	--	123.8	--	--	--
1350	--	--	374.4	--	124.9	--	--	--
1400	--	--	397.4	--	125.9	--	--	--
1450	--	--	421.7	--	126.9	--	--	--
1500	--	--	446.0	--	127.8	--	--	--

* Thermal conductivity values extrapolated in the range of transformation or anomalous behavior in parentheses.

4.2. Specific Heat

Specific heat measurements of zirconium alloys were subject to even greater difficulties than thermal diffusivity experiments. The applied direct pulse heating method relies on contact temperature measurement, and all the difficulties described in relation to thermal diffusivity were present in these measurements too. A total of 31 experiments was performed, in which the experimental conditions, such as heating rates, thermocouple wire dimensions, and specimens, were varied.

A range of thermocouple types and techniques of fixing thermocouples to the specimen was used to achieve measurements above 1000 C, as irrespective of the speed of measurement, the contact between the spot-welded thermocouple and the specimen substrate broke approximately in the range above 1000 C. In the range below 1000 C, both K-type and S-type 0.05-mm-diameter thermocouples demonstrated good performance.

Above 1000 C, the only acceptable results were obtained using a 0.1-mm-diameter W5% Re/W26% Re thermocouple embedded and peened in the hole 0.3 diameter and 0.5 mm deep. Peening ensured good thermal and electric contact between the specimen material and the thermocouple leads from the hole virtually in the same radial plane. Parallel temperature measurements in the same experiment with a welded K-type thermocouple provided *in situ* calibration of the tungsten/rhenium thermocouple, up to the temperature at which the former lost its contact with the substrate. The peening technique and the 0.1-mm-diameter thermocouple could, for obvious reasons, be used only with a 4-mm-diameter specimen. This technique in turn enabled extension of specific heat and electrical resistivity measurements to 1500 C.

Due to the difficulties encountered in the pulse calorimetry measurements, considering small differences in chemical composition and their possible consequences on measured specific heat, Zircalloy 2 was the only Zircalloy on which successful measurements were performed. Altogether 33 experiments with the S-type thermocouple and seven with the W/Re thermocouple were made. Only the last 10 obtained with the S-type thermocouple and 4 with the W/Re thermocouple were taken into account for final processing. Of these four, in only one experiment was the maximum measuring temperature reached. The resulting specific heat function is presented in Fig. 3 and in Table I.

Measurements on Inconel 625 again posed no problems, and its specific heat function is given in Fig. 4 and in Table I.

4.3. Electrical Resistivity

Electrical resistivity was measured in the same experiments in which specific heats of Zircalloy and Inconel 625 were determined. Agreement

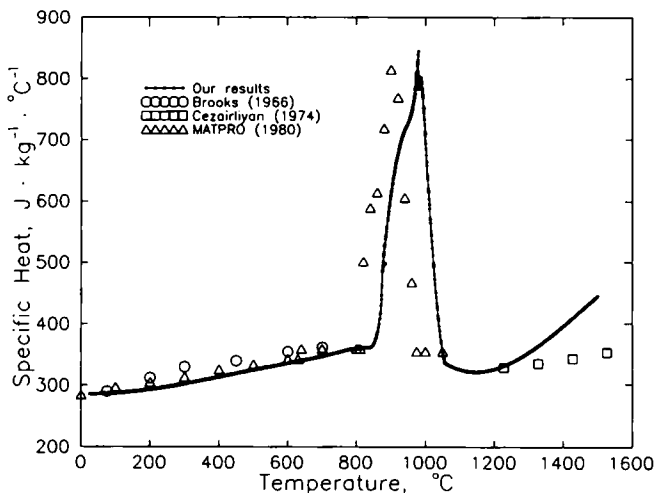


Fig. 3. Specific heat of Zircalloy 2.

between individual measurements was very good, deviations from the smoothed curves obtained by spline-fit averaging being within $\pm 0.1\%$. The final electrical resistivity functions of Zircalloy 2 and Inconel 625 are presented in Figs. 5 and 6, respectively, and the values at regular intervals are given in Table I.

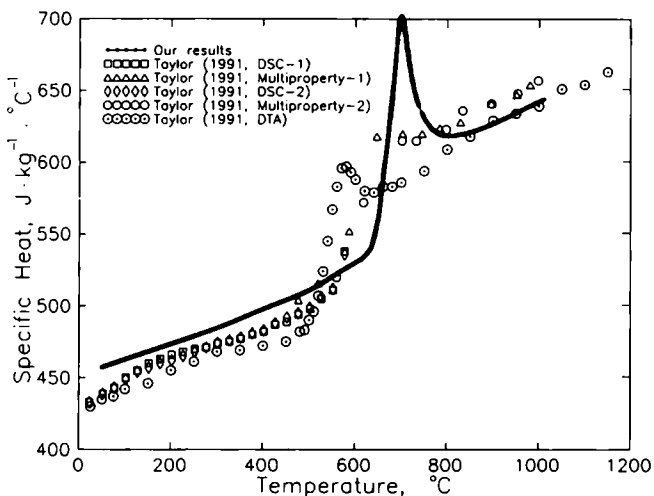


Fig. 4. Specific heat of Inconel 625.

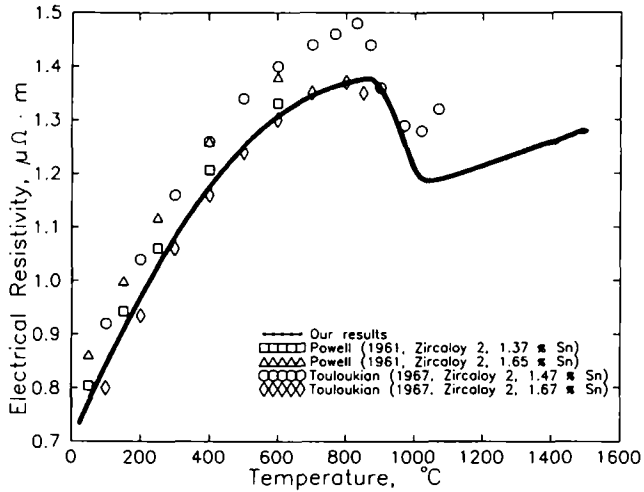


Fig. 5. Electrical resistivity of Zircaloy 2.

4.4. Thermal Conductivity

From smoothed thermal diffusivity function and interpolated thermal diffusivity values, specific heat values, and room temperature densities, D , determined from separate experiments, thermal conductivities of Zircalloy

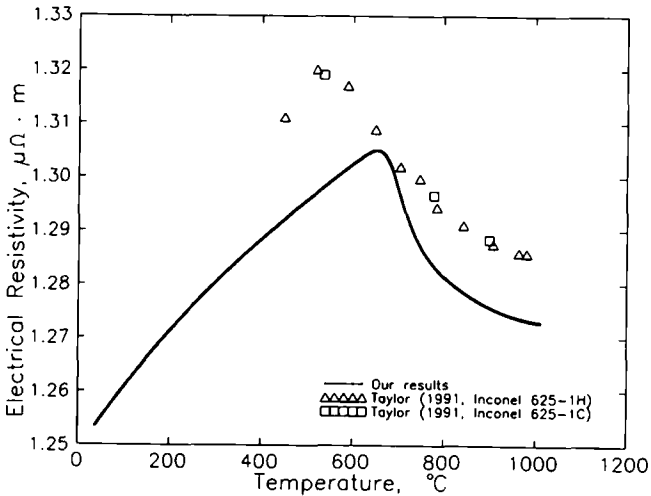


Fig. 6. Electrical resistivity of Inconel 625.

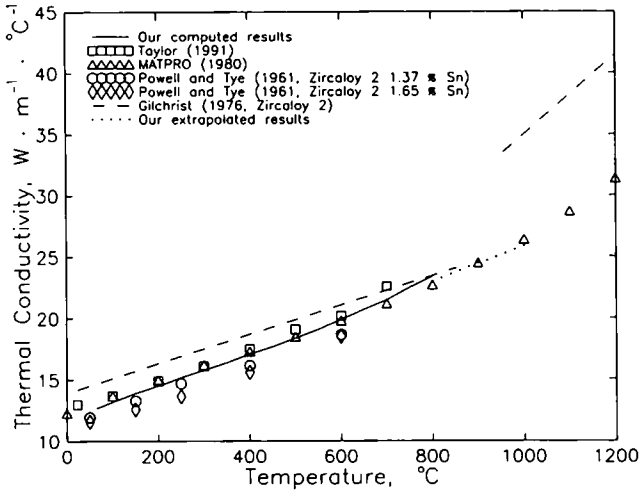


Fig. 7. Thermal conductivity of Zircalloy.

and Inconel 625 were computed according to the relation: $\lambda = Dac_p$. Thermal conductivity functions of Zircalloy and Inconel 625 are shown in Figs. 7 and 8, respectively, and the values are given in Table I. Due to the absence of our thermal expansion data, thermal conductivities at elevated temperatures were not corrected for changes in density.

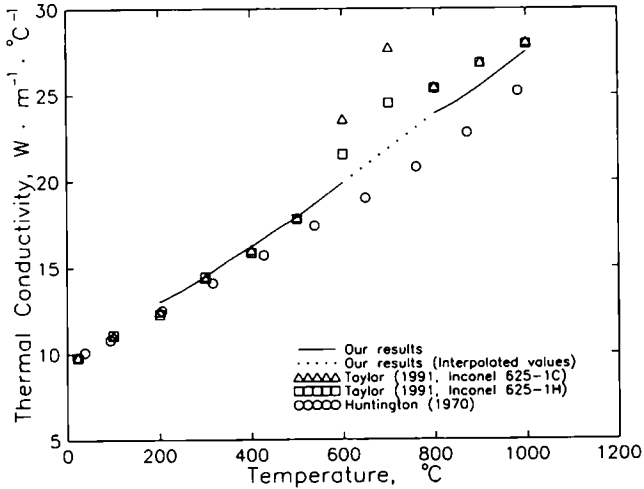


Fig. 8. Thermal conductivity of Inconel 625.

5. DISCUSSION

5.1. Zircalloy

The difference of approximately 1% between our thermal diffusivity results obtained for Zircalloy 2 and those for Zircalloy 4 (presented in Fig. 1) implies that the results obtained for the two alloys lie virtually within the limits of the experimental accuracy. It therefore seems unnecessary to consider these as the two separate sets of experimental results, and the thermal diffusivity of Zircalloy can be represented by the following functions:

$$a = 6.77895 + 0.00212061t + 1.58106 \times 10^{-6}t^2 \quad (\text{for } 20 \leq t \leq 850 \text{ C}) \quad (4)$$

and

$$a = -67.2272 + 0.150144t - 6.9991 \times 10^{-5}t^2 \quad (\text{for } 850 \leq t \leq 1000 \text{ C}) \quad (5)$$

As described in Section 3.1, the laser pulse facility and the technique applied did not permit measurements above 1000 C.

Comparison between our thermal diffusivity data and the TPRL data [4] shows very good agreement in the range up to approximately 900 C, where the results start to diverge somewhat. Difficulties in our measurements close to 1000 C and scatter of the results could explain the divergence in this region.

Figure 1 also shows thermal diffusivity data computed from the Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior (MATPRO)-recommended thermal conductivity function [5] and our specific heat function. The difference between computed MATPRO values and our and TPRL values is 7% at 100 C, and reduced to 5% at 800 C, where the MATPRO function ends. The MATPRO points lie in the whole range above the two other sets. When the MATPRO function is linearly extrapolated to 1000 or 1100 C, which is usually done in engineering calculations, a more striking difference is obtained. Then the difference becomes some 23%, with MATPRO-extrapolated data lying below our and the TPRL data.

Two other data sets, reported by Gilchrist [6] and Bunnell et al. [7], lie above and below the three data sets discussed above. Data reported by Gilchrist [6] do not cover the range between 845 and 910 C, while the lower-positioned function proposed by Bunnell et al. (in their study of the influence of oxygen on zirconium alloys) in the said region displays a shape similar to our and the TPRL data. The thermal diffusivity functions for Zircalloy 2 and Zircalloy 4 reported by Peggs et al. [8] in the 150-800 C

region represented a direct linear extrapolation backward of the Gilchrist high-temperature data (910–1200 C), lying above our interpolated function by 10% at 200 C and by 26% at 800 C. This set is not shown in Fig. 1.

The argument about a single set of results representing both Zircalloy alloys holds for specific heat also, as the specific heat is even less sensitive to a small variation in the composition of the alloying elements than are the transport properties. Figure 3 shows our data and the data of Brooks and Stansbury [9] and Deem and Eldridge [10] (the latter being the base for the MATPRO's recommended function for specific heat data). Agreement is generally good except in the position of α - β transformation of zirconium, which in our experiments occurs at a somewhat higher (by about some 40 C) temperature. Our experiments using all three types of thermocouples have confirmed this position of transformation on the temperature scale, and W/Re thermocouples enabled extension of the specific heat data for Zircalloy to above 1500 C. Figure 3 also contains the lower portion of the high-temperature specific heat data for zirconium reported by Cezairliyan [11].

Figure 5 shows the electrical resistivity function obtained in our experiments with Zircalloy 2 covering the range from room temperature to above 1500 C. The figure also displays two literature data sets reported for Zircalloy 2 having different Sn contents (1.47 and 1.67%) [12]. Measurements of the electrical resistivity of two zirconium alloys with 1.37% Sn and 1.65% Sn were reported by Powell and Tye [13] in the 50–600 C range; their data for the 1.37% alloy are between 4 and 2% and those for 1.65% alloy are some 11 to 6% above our curve.

Figure 7 presents the thermal conductivity function of Zircalloy computed from our thermal diffusivity smoothed function, specific heat data, and room-temperature density measurements. As both the thermal diffusivity and the specific heat display an effect of α - β transformation in zirconium, the thermal conductivity has been linearly extrapolated in the region between 800 and 1000 C; otherwise, the thermal conductivity would display a hump equal to the product of these two effects, which is in discord with the physical nature of thermal conductivity. Other thermal conductivity data presented in Fig. 7 are these of TPRL [4], UKAEA [6], and MATPRO [5] recommended thermal conductivity data. General agreement among them, from room temperature to 1200 C, is reasonably good.

5.2. Inconel 625

Our thermal diffusivity data obtained for Inconel 625 shown in Fig. 2 display a good agreement with the TPRL results [4]. The manufacturer's

data [14] are in good agreement with the above to 200 C, above which temperature they start to diverge. Being computed from thermal conductivity experiments, they naturally cannot display the anomaly which appears in the 700–800 C region.

Good agreement exists also between our Inconel 625 specific heat results and the TPRL results obtained by three techniques, using multiproperty apparatus calorimetry, differential scanning calorimetry, and differential thermal analysis. The difference is only in the position and the shape of the anomaly.

Our experimental results of all property measurements realized on Inconel 625 samples reveal an anomaly in the range near 700 C. The maximum of thermal diffusivity lies between 690 and 700 C, and the specific heat function reaches its maximum between 700 and 720 C. The electrical resistivity function shows a maximum at 691 C, the minimum of its derivative function, $dp/d\theta$, being at 720 C. The explanation that this anomaly is heating rate dependent, similar to some other nickel alloys, Nichrome 5 [15], and austenitic stainless steel 1.4970 [16], is not very likely, as the same position has been confirmed by virtually nondynamic thermal diffusivity measurements. On the other hand, the TPRL measurements carried out in 1991 locate the anomaly at a temperature some 100 C lower. Since the specimens were the same and the measurements at two laboratories agree well outside the anomaly range, it is possible that in the meantime the material has undergone some structural ordering. As the final objective of this research is the establishment of recommended property functions, this phenomenon deserves further consideration.

The difference in the shape of the anomaly in the specific heat is not critical. In our dynamic experiments, the sampling rate is kept constant throughout the experiment, resulting in a reduced number of data points near transitions and, consequently, in a lower accuracy for specific heat measurements in these regions. In the particular studies of phase transitions or anomalies, much bigger sampling rates are used in the critical regions, but this was not the case with Inconel 625. The shape of the anomaly might therefore be better described by DSC, multiproperty (MP), or DTA measurements carried out at TPRL.

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