

Zircaloy Heat Capacity

Recommendations

The recommended equations for the heat capacity of Zircaloy in the α -, β -, and combined ($\alpha + \beta$)- phases are based on least square fits to the available data on the heat capacity of Zircaloy-2 [1-9], which are listed in Table 1. No measurements of the heat capacity of Zircaloy-4 have been found in the open literature.

The recommended equation for the heat capacity of Zircaloy-2 in the α - phase is:

For $273 \text{ K} < T < 1100 \text{ K}$,

$$C_p = 255.66 + 0.1024 T \quad (1)$$

where temperature is in K and heat capacity is in $\text{J kg}^{-1} \text{ K}^{-1}$.

The recommended equation for the heat capacity of Zircaloy-2 in the β - phase is the quadratic equation obtained by Righini et al.[6] from fitting their β - phase data.

For $1320 \text{ K} < T < 2000 \text{ K}$

$$C_p = 597.1 - 0.4088 T + 1.565 \times 10^{-4} T^2 \quad (2)$$

where temperature is in K and heat capacity is in $\text{J kg}^{-1} \text{ K}^{-1}$.

The Zircaloy-2 heat capacity data in the ($\alpha + \beta$)- phase-transition region of Righini et al.[8] have been fit by a Gaussian function plus the equations for the dominant α - or β - phase. This Gaussian function is

$$f(T) = 1058.4 \exp\left[\frac{(T-1213.8)^2}{719.61}\right] \quad (3)$$

where temperature is in K and heat capacity is in $\text{J kg}^{-1} \text{ K}^{-1}$. From 1100 K through 1214 K, the

recommended values for the heat capacity of Zircaloy-2 are obtained from the sum of Eq.(1) + Eq.(3). From 1214 to 1320 K, the recommended values for the heat capacity of Zircaloy-2 are obtained from the sum of Eq.(2) + Eq.(3). Recommended values for the heat capacity of Zircaloy-2 are tabulated in Table 2, and shown in Figure 1.

Uncertainty

The two-standard deviation uncertainty for the recommended Zircaloy-2 α -phase heat capacities is 2-3%. The errors in the regression coefficients for 95% confidence, which is an uncertainty of two standard deviations, are:

$$C_p = (255.66 \pm 3.75) + (0.10240 \pm 0.00537) T \quad (4)$$

The uncertainties for the α -phase heat capacities calculated from Eq.(4) are shown as dotted lines in Figure 2, which shows the recommended values (solid line) and the experimental data. These uncertainties for the α -phase heat capacities are consistent with an uncertainty of $\pm 10 \text{ J kg}^{-1} \text{ K}^{-1}$ (3%) given in MATPRO[10].

The estimated uncertainty in the recommended values for Zircaloy-2 heat capacity in the β -phase is 10% ($\sim \pm 30 \text{ J kg}^{-1} \text{ K}^{-1}$) from 1300 K to 1600 K and increases linearly to 20% ($\sim \pm 70 \text{ J kg}^{-1} \text{ K}^{-1}$) at 1700 K and higher temperatures. These uncertainties are greater than the root mean square of the sum of the squares of the errors given by Righini et al.[6] for the imprecision in the fit (1.2%) and inaccuracy (4%) in the heat capacity measurements but they are much less than the $\pm 100 \text{ J kg}^{-1} \text{ K}^{-1}$ uncertainty given by MATPRO [10] for the constant heat capacity recommended by MATPRO for this phase. In Figure 3, the recommended values and uncertainties are compared with the data of Righini et al.[6], of Maglic et al.[9] and the constant β -phase heat capacity given in MATPRO [10]. The larger uncertainty than the 4% obtained from statistical analysis of the known analytical and experimental errors of Righini et al.[6] is warranted because the data of Deem and Eldridge [1] deviates by 10% from that of Righini et al.[6] and above 1600 K, the data of Maglic et al. [9] deviates by more than 10% from that of Righini et al.[6].

The uncertainty in recommended values for the ($\alpha + \beta$) - transition phase is estimated as 10%, which is larger than the uncertainty of $\pm 25 \text{ J kg}^{-1} \text{ K}^{-1}$ given in MATPRO. This larger uncertainty reflects the disagreements in the heat capacity phase transition data of three different investigators [1,8, 9] and the sensitivity of the phase transition temperature and the heat capacity in the two-phase region to the temperature history of the samples (such as annealing) that was found by Righini et al.[8] It is consistent with the 10% variation in the total energy absorbed during the phase transition that was found by Righini et al. for samples with different thermal histories that were heated using different heating rates. The phase transition temperature and the heat capacity in the two-phase region are also very sensitive to oxygen content. Thus, even larger uncertainties may be appropriate if oxygen dissolution in the Zircaloy is suspected and the amount of oxygen in the Zircaloy is not known.

Uncertainties for application of the Zircaloy-2 heat capacity equations to Zircaloy-4 are 20% for the α -phase and 30% for the ($\alpha + \beta$) - transition phase and the β -phase. These uncertainties are based on the absence of data for Zircaloy-4 and the differences between measured Zircaloy-2 heat capacities and Zircaloy-4 heat capacity values calculated from measurements of thermal diffusivity, thermal conductivity, and thermal expansion.

Discussion

Phases

Unlike zirconium, which has a sharp $\alpha \rightarrow \beta$ transition at 1139 K, Zircaloy has no sharp change from the α - phase to the β - phase but has a two-phase ($\alpha + \beta$) region. For Zircaloy-2, the temperature range for this transition given by Bunnell et al.[11] is 1083 to 1223 K. However, Righini et al.[8] found that the coexistence region ranges from 1050 K to 1400 K and the exact temperature range depends on the sample's thermal history and heating rate. The phase boundaries are also a function of dissolved oxygen in the sample. The effect of dissolved oxygen on the α - and β - phase boundaries of the ($\alpha + \beta$) two-phase region in Zircaloy-4 has been studied by Chung et al.[12,13]. The effect of dissolved oxygen in Zircaloy-2 on these phase boundaries has been studied by

Rubenstein et al.[14], Mallet et al.[15], Ostberg [16] and Chung et al. [12,13]. Dissolved oxygen stabilizes the α - phase to higher temperatures and produces a broader two-phase ($\alpha + \beta$) region.

α - Phase Heat Capacity

Table 1 lists the available data for the heat capacity of Zircaloy-2. Most of the available data are for the α - phase. In Figure 4, the Zircaloy-2 heat capacity data for the α - phase are compared with the MATPRO[10] recommended values, which are based on the 1966 measurements of Brooks and Stansbury [2]. Since the MATPRO assessment, new heat capacity measurements have been made by six experimental groups and their data are not consistent with the MATPRO recommendation. Therefore, the α - phase Zircaloy-2 heat capacity data have been reanalyzed. Righini et al. [8] studied the effect of annealing and heating rate on the heat capacity in the α - phase. Their results for as received samples (s1 and s2) showed no significant difference from their sample s3, which was annealed at 1300 K in a high vacuum for one hour. Heat capacities obtained from experiments with slow and fast heating rates on two annealed samples showed variations of $\pm 0.1\%$ to $\pm 1.1\%$ with no systematic trends. Thus, Righini et al.[8] concluded that the heat capacity of Zircaloy-2 in the α - phase does not depend on either the heating rate or the thermal history of the sample. Consequently, all the α - phase data from the measurements shown in Table 1 have been analyzed together.

A least squares fit of these data showed that they are well represented by a linear equation. Equation (1) fits the 247 heat capacity data in the α - phase with a multiple correlation coefficient, R, of 0.92. This recommended equation is compared with the MATPRO recommended values and the available α - phase data in Figure 5. Percent deviations of the data from this equation defined by

$$Deviation(\%) = \frac{[C_p(Data) - C_p(Recommended)]}{C_p(Recommended)} 100\% \quad (5)$$

are shown in Figure 6. Data from measurements by Murabayashi et al.[3] are 4 to 7% higher than the recommended values while data from measurements by Gilchrist [5] are low by 2 to 11%.

Deviations for other data are mainly $\pm 4\%$ or less. Data of Casey and Yates [4], of Righini et al. [8] and of Deem and Eldridge [1] are all within $\pm 2\%$ of the recommended equation. Except for the data of Casey and Yates [4], of Righini et al. [8] and of Deem and Eldridge [1], the data by each experimenter is consistently high or low, indicating the deviations are systematic.

β - Phase Heat Capacity

Only the data of Deem and Eldridge [1], of Righini et al.[6,8] and of Maglic et al. [9] extend beyond the α - phase and through the phase transition region. The Deem and Eldridge data do not extend far enough into the β - phase to provide information on the temperature dependence in this phase. The β - phase data of Maglic et al. [9] and that of Righini et al.[6] have significantly different temperature behavior. Consequently, a combined fit of these data is not recommended. Measurements by Righini et al.[6] were on as received samples, which had no annealing, and were well characterized with respect to composition and density. The data reported by Righini et al. [6] are the averages of seven measurements on specimen-1, four experiments for specimen-2, and five experiments for specimen-3. Three different heating rates were used for each specimen to determine if heating rate effected the measured property. No dependence on heating rate was observed for the heat capacity in the β - phase. Measurements by Maglic et al.[9] were on samples annealed in a vacuum at 823 K. Maglic et al.[9] reported considerable difficulty with measurements at high temperatures using both Type-S and W/Re thermocouples. Of thirty-three experiments, only fourteen were considered reliable and only one of these reached the maximum temperature reported. Thus, the data of Maglic et al.[9] in the β - phase are not considered to be as reliable as the data of Righini et al.[6] Therefore, the quadratic equation obtained by Righini et al. from their least squares fit to their data is recommended. The relative standard deviation of an individual data point from their recommended equation, Eq.(2), is 1.2%. This equation is shown with uncertainties in Figure 3 along with the MATPRO [10] constant heat capacity, the data of Righini et al.[6] and the data of Maglic et al.[9].

Heat Capacity in the Phase Transition Region

The effects of previous thermal history and heating rate on the temperature limits of the phase transition and on the heat capacity in the phase transition region have been extensively studied by Righini et al.[8, 17] for Zircaloy-2 and by Peletsky et al.[18,19] for Zr-1%Nb. Righini et al.[8] found that both the heat capacity and the temperature limits of the phase transition have a strong dependence on the thermal history of the sample and a weak dependence on heating rate. Differences in the phase-transition region heat capacities for as received and annealed samples of Zircaloy-2 obtained by Righini et al. [8] during their first heating cycle are shown in Figure 7. Table 3 gives the thermal history of each sample referred to in Figure 7. Heat capacities for the two as received samples (s1a, s2a) are similar with a narrow peak just above 1210 K. The annealed samples show greater variation with wider lower peaks at temperatures that are higher by 20 to 25 K. Righini et al.[8] observed consistent differences between the first heating cycle and subsequent cycles. In general, the presence of the sample in the β - phase (either from annealing or from previous measurements) creates a wider temperature range for the phase transformation with respect to as-received samples. Measurements after the first heating cycle tended to be reproducible. In their study of the kinetics of the phase transformation in Zircaloy-2, Corchia and Righini [17] found that the kinetics are a function of the microstructure of the sample, which is dependent on the thermal and metallurgical history. Experiments after the first cycle tend to be reproducible because the pulse heating through the phase transition changes the microstructure of the sample,

In their study of effects of heating rate, Righini et al.[8] showed that the shape of the heat capacity curve is maintained in slow and fast experiments but the phase-transition peak in slow experiments tends to be lower by 10 to 20 K. Figure 7 shows that the heat capacity data of Deem and Eldridge [1] that was obtained by isothermal calorimetry have a wide peak that is shifted toward lower temperatures with a shape similar to the curves obtained by Righini et al. [8] after the first heating cycle. Righini et al.[8] commented that this shift to low temperatures is consistent with the very low heating rate for equilibrium calorimetry. This shift of the phase-transition peak in zirconium alloys to low temperatures during slow heating was confirmed by Lusternik et al.[18], who measured the

heat capacities of Zr-1%Nb in the phase-transition region using both a subsecond pulse heating method (heating rate of 2000 K s^{-1}) and by adiabatic calorimetry (heating rate of 0.02 K s^{-1}). Figure 7 shows that the peak of the heat capacity data of Maglic et al. is shifted to higher temperatures. This is consistent with the observation of Righini et al.[8] that annealing and/or repeated cycling through the β - phase shifts the heat capacity peak to higher temperatures (see sample s3N2). The shape of the peak of the data of Maglic et al. is similar to the peak obtained by Deem and Eldridge.

For ten measurements on samples with different thermal histories and different heating rates, Righini et al.[8] integrated the heat capacities in the phase transition region (from 1050 K through 1390 K) to determine the total absorbed energy of the transition for each sample. The total absorbed energy ranged from 188.5 J g^{-1} to 207.8 J g^{-1} with no discernable trend. Thus, although the location of the phase transition peak and the shape of the peak differs in accord with the thermal history of the sample, the absorbed energy difference is within 10%. So use of Zircaloy-2 heat capacity values in this transition region from a sample with a different thermal history than that of the material in a nuclear reactor would give an uncertainty of about 10% in the total heat needed to heat Zircaloy -2 from the α - phase to the β - phase during a reactor accident. For the nonequilibrium conditions of a nuclear reactor accident, Righini et al.[8] recommend using their heat capacities for the as received samples during their first cycle of heating (s1a, s2a).

To obtain equations for the heat capacities in the two-phase region that are consistent with recommended equations for the α - and β - phases, a non-linear least-squares minimization was used to determine a Gaussian function to represent the increase in heat capacity peak given by the heat capacity data of samples s1a and s2a (as received - first heating cycle) of Righini et al.[8] The phase transition data from 1133 to 1353 K of Maglic et al. and that of Deem and Eldridge above 1083 K were not included in this analysis because they are not consistent with heat capacity measurements on a first cycle of as received samples at a heating rate consistent with a reactor accident conditions. In this least squares minimization, the α - phase (273 - 1100 K) was represented by the linear equation Eq.(1), the β -phase (1320 - 2000 K) was represented by the

quadratic equation Eq.(2), and the combined phase was represented by a Gaussian function plus Eq.(1) up to the phase transition peak and a Gaussian function plus Eq.(2) from the phase-transition peak to the end of the transition region. The parameters for the Gaussian function (including the temperature for the peak and the width of the Gaussian) and the temperature ranges for the linear and quadratic equations in the two-phase region were free to vary in this non-linear least squares minimization. The best fit was obtained with the Gaussian function given in Eq. (3) for the temperature range from 1100 to 1320 K, the linear equation [Eq.(1)] from 273 to 1213.8 K, and the quadratic equation [Eq.(2)] from 1213.8 to 2000 K. Thus, the Zircaloy-2 heat capacities in the transition region are represented by the sum of Eq.(1) + Eq.(3) from 1100 K to 1214 K and by the sum of Eq.(2) + Eq.(3) from 1214 K to 1320 K. The recommended equations from 273 to 2000 K are shown in Figure 8 with the data and the MATPRO recommendation for comparison.

Zircaloy-4

No measurements of the heat capacity of Zircaloy-4 have been found in the open literature. However, Bunnell et al. [11] have calculated the heat capacity of Zircaloy-4 from their measurements of the Zircaloy-4 thermal expansion, thermal conductivity, and thermal diffusivity because they found that the constant heat capacity recommended by MATPRO [10] for the β -phase was inconsistent with their thermal conductivity and thermal diffusivity measurements. Their calculated heat capacities for Zircaloy-4 are shown in Figure 9 and compared with the Zircaloy-2 data and the recommended equations for the heat capacity of Zircaloy-2. The temperature dependence of their calculated Zircaloy-4 heat capacities is similar to that of the Zircaloy-2 data but the magnitude of the Zircaloy-4 heat capacities is higher. It is not clear if the higher values are real or due to the calculation. Until measurements of the heat capacity of Zircaloy-4 are available, the Zircaloy-2 equations are recommended with the caution that the actual heat capacities for Zircaloy-4 may be higher by 10 to 20% in the α - phase and by 30% in the β - phase. Thus the uncertainties for application of the Zircaloy-2 heat capacity equations to Zircaloy-4 should be significantly higher. The estimated uncertainties are 20% for the α - phase and 30% for the combined phase and the β -phase.

References

1. H. W. Deem and E. A. Eldridge, USAEC Report **BMI-1644** (1963), as tabulated and referenced by Y. S. Touloukian et al., *Thermophysical Properties of Matter Volume 4: Specific Heat Metallic Elements and Alloys*, p. 502-503, Plenum, New York (1970). See also H. W. Deem and E. A. Eldridge, *Specific Heats and Heat of Transformation of Zircaloy-2 and Low Nickel Zircaloy-2*, USAEC Report **BMI-1803** (May 1967).
2. C. R. Brooks and e. E. Stansbury, *The Specific Heat of Zircaloy-2 from 50 to 700 °C*, J. Nucl. Mater. **18**, 233-234 (1966).
3. M. Murabayashi, S. Tanaka, and Yoichi Takahashi, *Thermal conductivity and Heat Capacity of Zircaloy-2, -4, and Unalloyed Zirconium*, J. Nucl. Sci. Technol. **12**, 661-662 (October 1975).
4. D. N. Casey and B. Yates, *The Specific Heat Capacities of Boron-containing Alloys and Cermets of Zircaloy-2, and Related Thermodynamic Properties of Zirconium*, High Temp.-High Press. **6**, 33-46 (1974).
5. K. E. Gilchrist, *thermal Property Measurements on Zircaloy-2 and Associated Oxide Layers Up to 1200 °C*, J. Nucl. Mater. **62**, 257-264 (1976).
6. F. Righini, A. Rosso, and L. Coslovi, *Measurement of Thermophysical Properties by a Pulse-Heating Method: Zircaloy-2, 1320 to 2000 K*, Proceedings of the Seventh Symposium on Thermophysical Properties, Gaithersburg, Maryland, May 10-12, 1977, A. Cezairliyan ed., pp. 358-368, ASME (1977).
7. E. G. Price, *Thermal Conductivity, Electrical Resistivity, and Specific Heat of CANDU Constructional Alloys and AISI Type 403 End Fitting*, **TDVI-368** (1980), as tabulated and referenced by J. Cleveland, editor, *Thermophysical Properties of Materials for Water-Cooled Reactors*, IAEA **TECDOC-949** (1997).
8. F. Righini, L. Coslovi, and A. Rosso, *Measurement of Thermophysical Properties by a Pulse-Heating Method: The Phase Transformation of Zircaloy-2, (800 -1400 K)*, Proceedings of the Eighth Symposium on Thermophysical Properties, Gaithersburg, Maryland, June 15-18, 1981, J. V. Sengers, ed., Vol.II, pp. 51-61, ASME (1982).

9. K. D. Maglic, N. Lj. Perovic, and a. M. Stanimirovic, *Calorimetric and Transport Properties of Zircalloy 2, Zircalloy 4, and Inconel 625*, Int. J. of Thermophysics **15**, 741-755 (1994).
10. D. T. Hagrman, et al. *SCDAP/RELAP5/MOD 3.1 Code Manual MATPRO - A Library of Materials Properties for Light-Water-Reactor Accident Analysis*, USNRC Report **NUREG/CR-6150, EGG-2720 Vol. 4** (1995).
11. L. R. Bunnell, J. L. Bates, and G. B. Mellinger, *Some High-Temperature Properties of Zircalloy-Oxygen Alloys*, J. Nucl. Mater. **116**, 219-232 (1983).
12. H. M. Chung and T. F. Kassner, *Pseudobinary Zircalloy-Oxygen Phase Diagram*, J. Nucl. Mater. **84**, 327-339 (1979).
13. H. M. Chung, A. M. Garde, and T. F. Kassner, in *Light-Water-Reactor Safety Research Program: Quarterly Progress Report, April-June 1975*, Argonne National Laboratory Report **ANL-75-58**, pp. 63-74 (1975).
14. L. S. Rubenstein, J. G. Goodwin, and F. L. Shubert, *Effect of Oxygen on the Properties of Zircalloy-2*, Transactions of the ASM **54**, 20-30 (1961).
15. M. W. Mallet, W. M. Albrecht, and P. R. Wilson, J. Electrochem. Soc. **106**, 181 (1959).
16. G. Osteberg, *Metallographic Study of Isothermal Transformation of Beta Phase in Zircalloy-2*, Jernkontoets Ann. **145** 119 (1963).
17. M. Corchia and F. Righini, *Kinetic Aspects of the Phase Transformation in Zircalloy-2*, J. Nucl. Mater. **97**, 137-148 (1981).
18. V. E. Lusternick, V. E. Peletsky, and I. I. Petrova, *High Temperature Calorimetric Measurements of Zr-0.01Nb Alloy at Various Rates of Heating*, High Temp.-High Press. **25**, 539-543 (1993).
19. V. E. Peletsky and I. I. Petrova, *Investigation of the Thermophysical Properties of the Alloy Zr-0.01Nb by a Subsecond Pulse-Heating Technique*, High Temp.-High Press. **29**, 373-378 (1997).

Table 1 Zircaloy-2 Heat Capacity Data

Experimenter	Ref	Year	Temperature (K)	No. of Points	Method	Comments
Deem & Eldridge	1	1963	273-1323	23	Isothermal Calorimetry	
Brooks & Stansbury	2	1966	323-973	91	Dynamic Adiabatic Calorimetry	97.1% Zr 1.29% Sn 0.012% O ₂
Casey & Yates	3	1974	300 - 570	38	Adiabatic Calorimetry	
Murabayashi et al.	4	1975	300-850	21	Laser Flash	98.2% Zr 1.49% Sn
Gilchrist	5	1976	298-1010	18	Differential Scanning Calorimetry	98.2% Zr 1.53% Sn
Righini et al.	6	1977	1320 - 2000	54	Pulse heating	98.08% Zr 1.42% Sn 0.154% Fe 0.125% Cr 0.052% Ni as received
Price	7	1980	340 - 675	36		Annealed & Cold-worked
Righini et al.	8	1981	800 - 1100 1040 - 1380	37 132	Pulse heating, slow & fast rates	as received samples & samples annealed at 1300 K
Maglic et al.	9	1994	298-1773	40	Millisecond-resolution direct electrical pulse heating	Annealed at 823 K in vacuum

Table 2 Recommended Values for the Heat Capacity of Zircaloy-2

Temperature, K	Heat Capacity, J/(kg K)
273	283.6
300	286.4
400	296.6
500	306.9
600	317.1
700	327.3
800	337.6
900	347.8
1000	358.1
1100	368.3
1120	370.4
1140	372.9
1160	393.3
1180	592.3
1200	1190.0
1210	1416.6
1214	1438.3
1220	1335.1
1240	739.3
1260	385.2
1280	332.7
1300	330.2
1400	331.5
1500	336.0
1600	343.7
1700	354.4
1800	368.3
1900	385.3
2000	405.5

Table 3 Thermal History of Heat Capacity Samples in Figure 7

Sample	Condition	Heating Rate
Righini s1a	as received	fast
Righini s2a	as received	fast
Righini s3n	annealed at 1300 K for 1 hr	fast
Righini s3n2	annealed at 1300 K for 1 hr; second annealing at 1300 K for 10 hrs	fast
Righini s4n	annealed at 1300 K for 10 hrs	slow
Deem & Eldridge	(repeated cycling ?)	slow (equilibrium)
Maglic et al.	annealed at 923 K, repeated cycling above 1300 K	fast

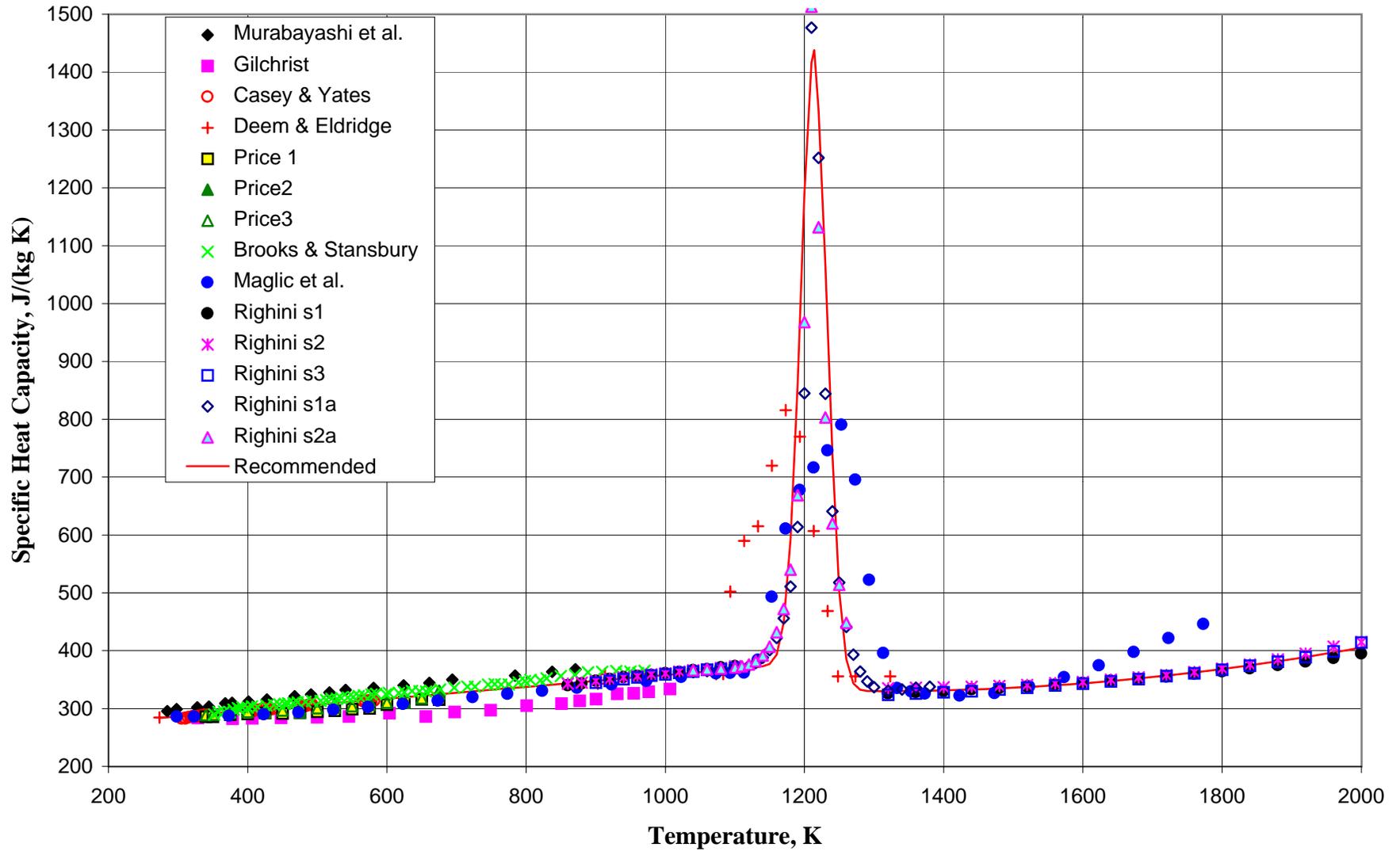
Fig. 1 Recommended Fit to Zircaloy-2 Heat Capacity Data

Fig. 2 Recommended Equation for the α -Phase Heat Capacity of Zircaloy-2

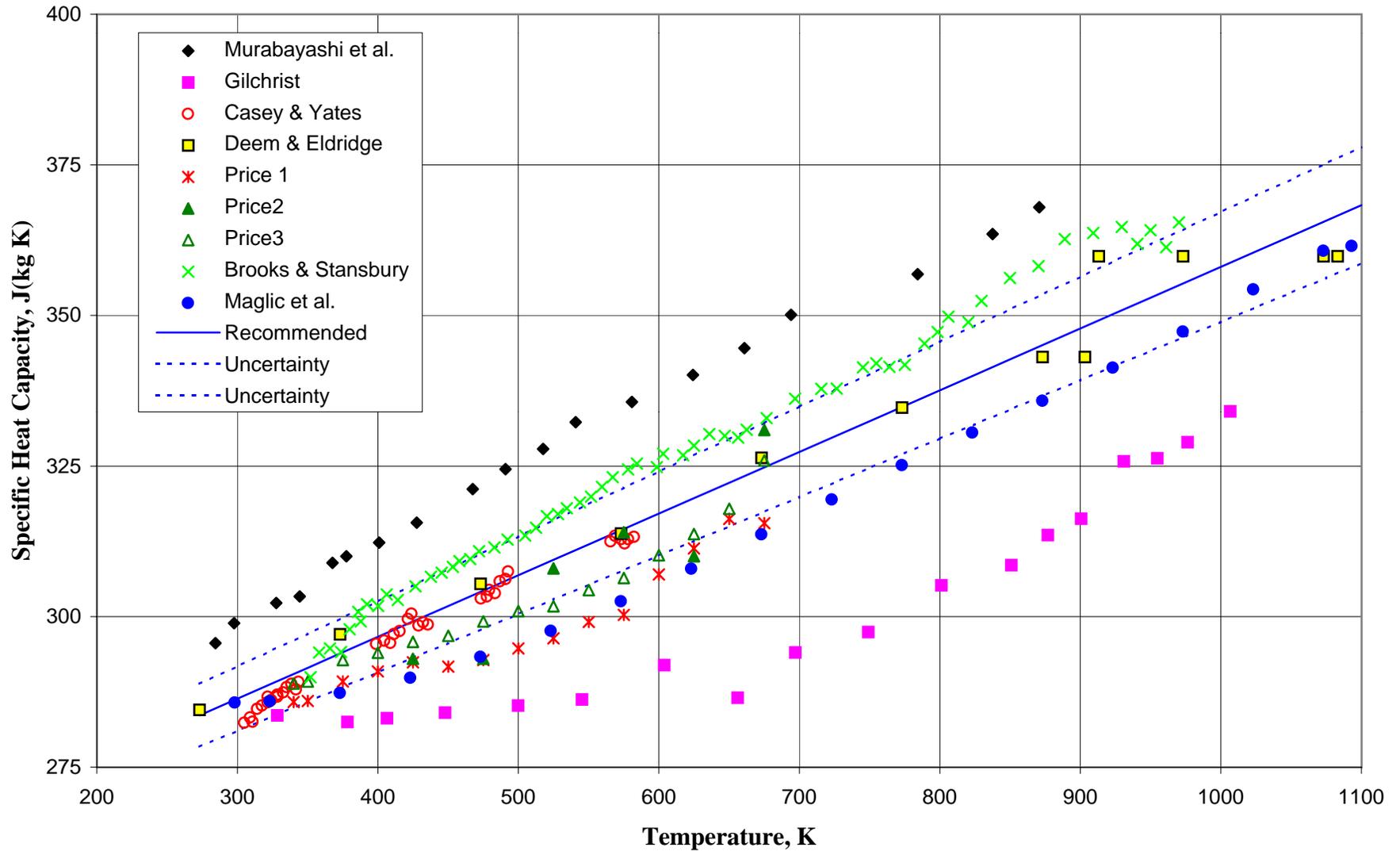


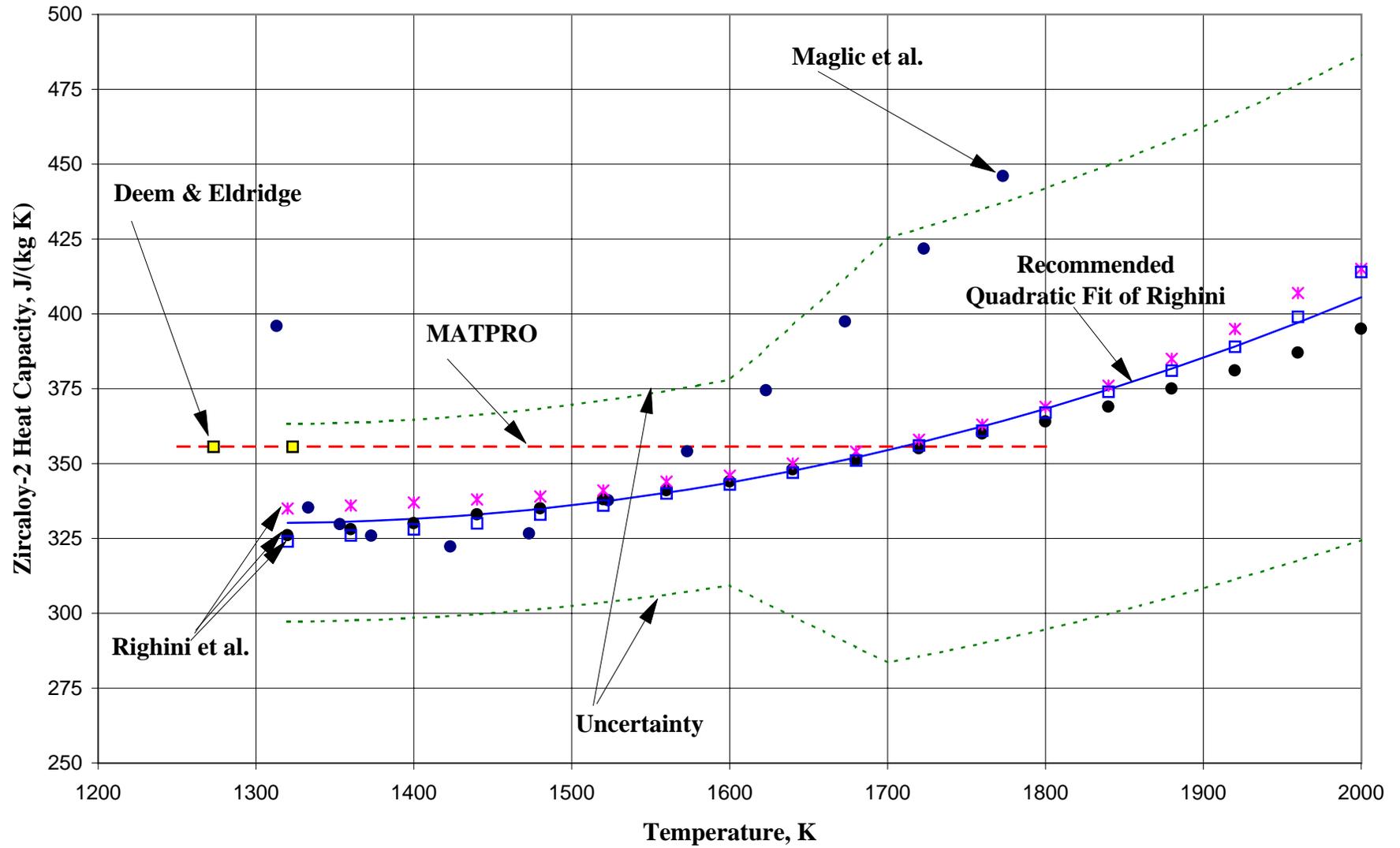
Fig. 3 Recommended Equation for the β -Phase Heat Capacity of Zircaloy-2

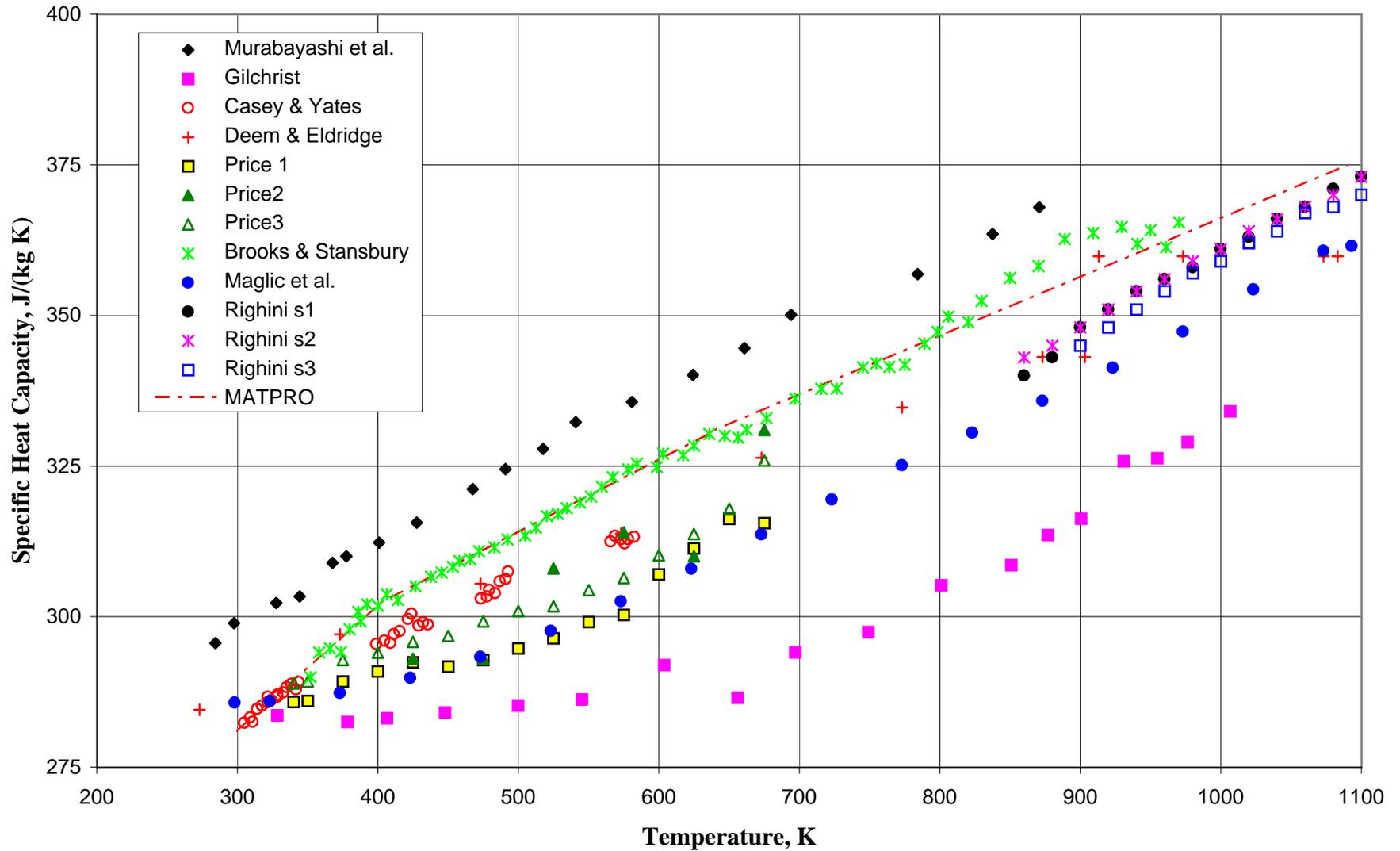
Fig. 4 Comparison of MATPRO Values with Zircaloy-2 α -Phase Heat Capacity Data

Fig. 5 Recommended Linear Fit to the α -Phase Heat Capacity of Zircaloy-2

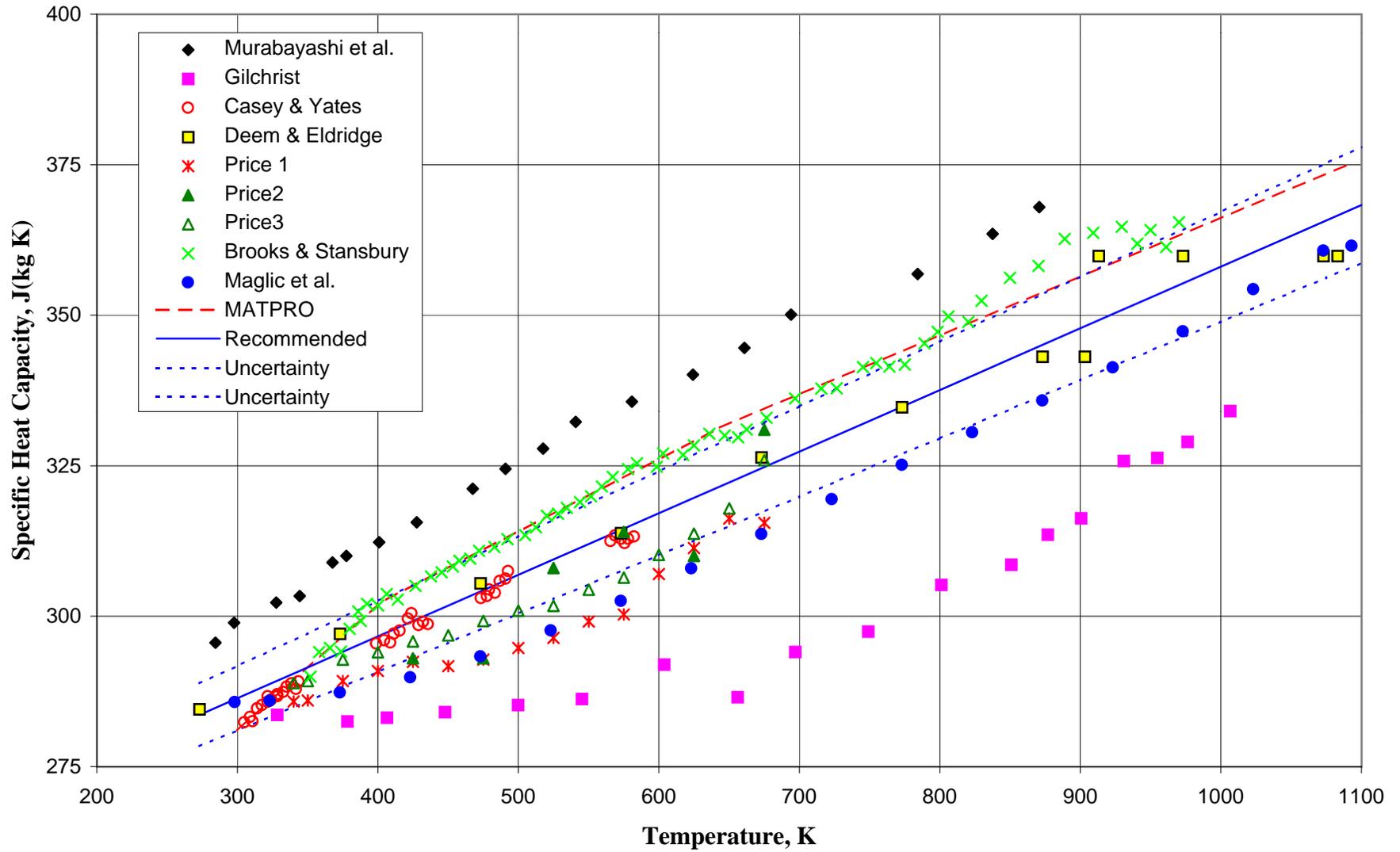


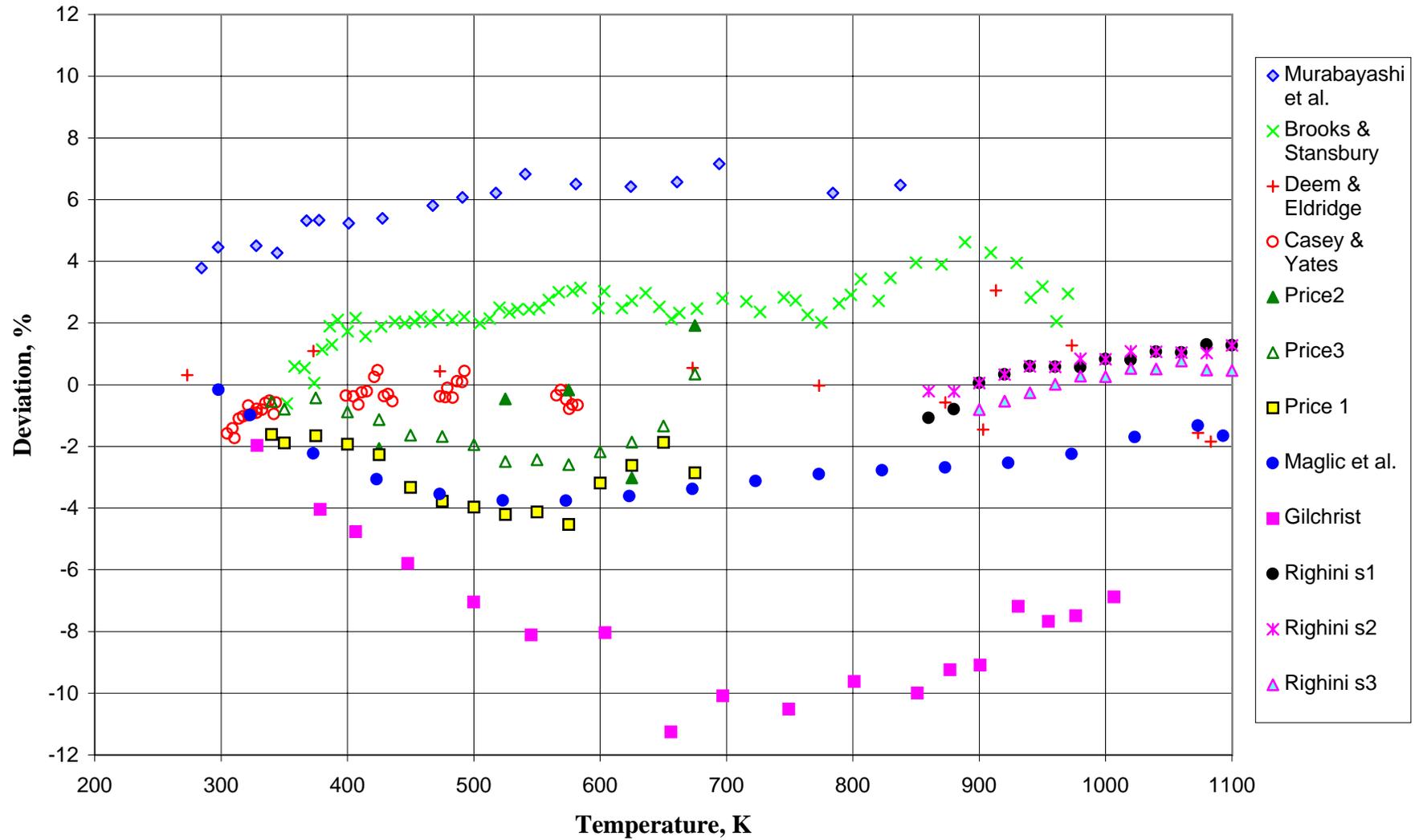
Fig. 6 Deviation of Zircaloy-2 Heat Capacity Data from Linear Equation

Fig. 7 Comparison of Heat Capacity Data in the Phase Transition Region

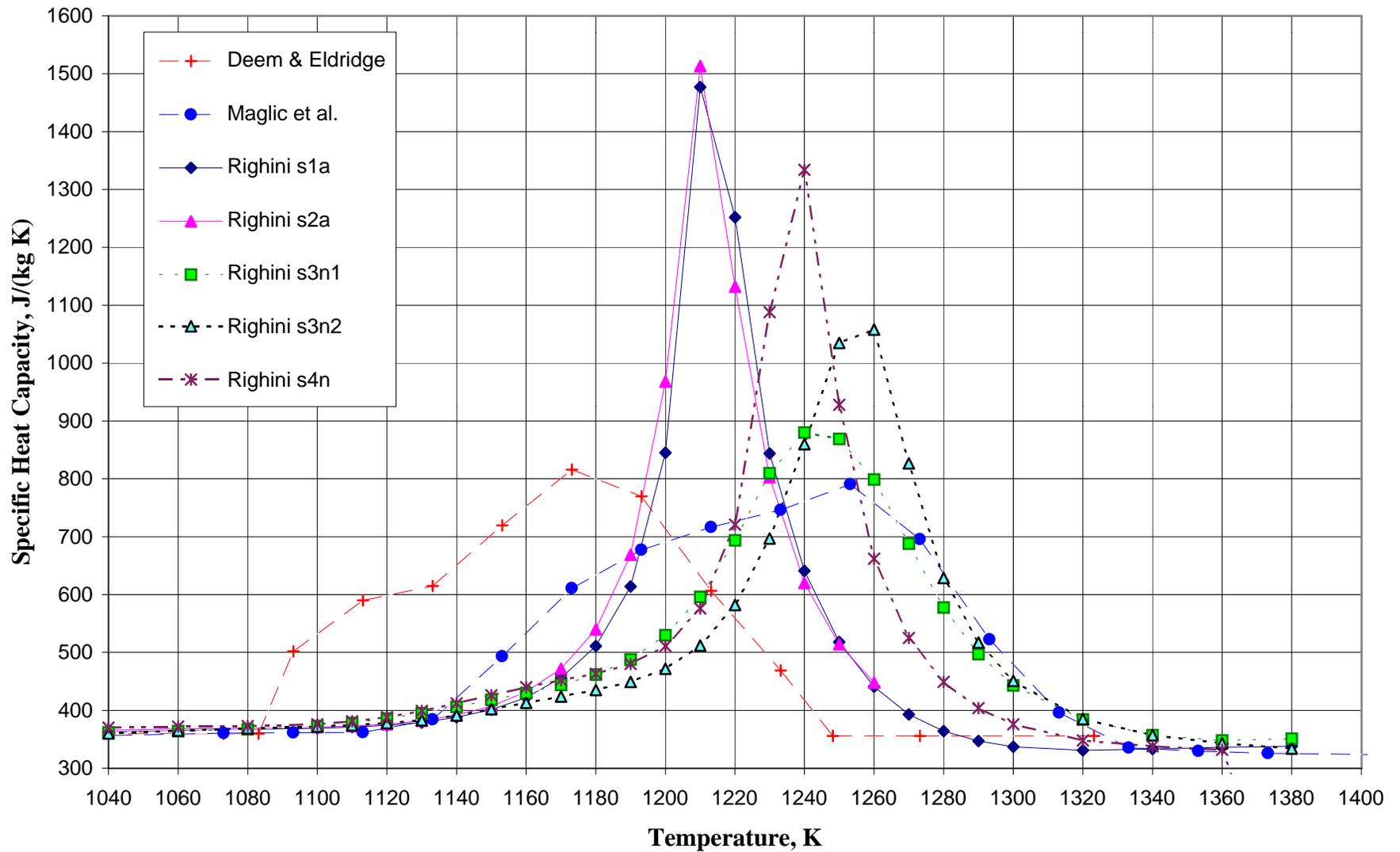


Fig 8 Comparison of MATPRO & Recommended Fit to Zircaloy-2 Heat Capacity Data

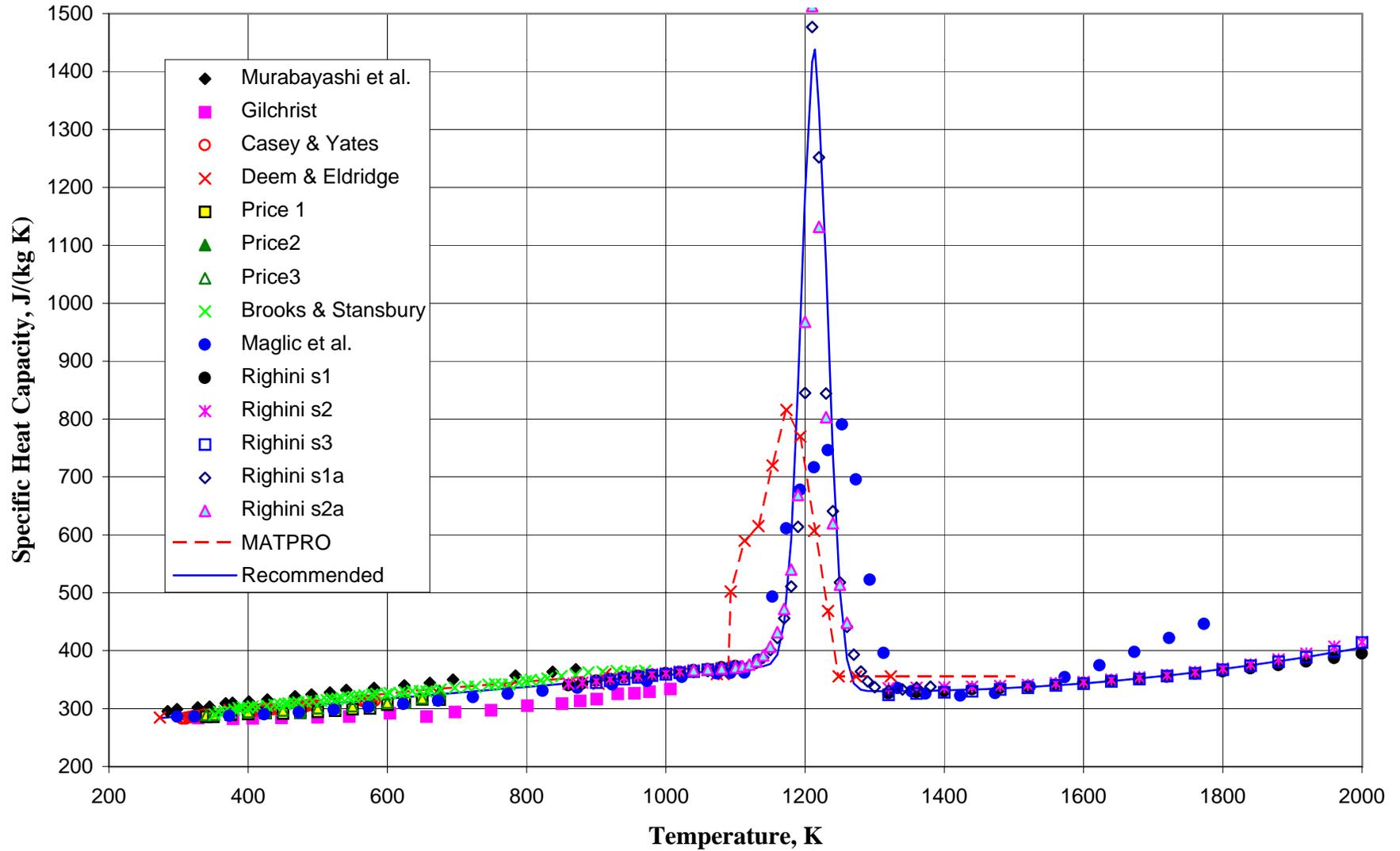


Fig. 9 Comparison Zircaloy-2 and Zircaloy-4 Heat Capacities

