

7.4

# The Characterisation of the Thermal Properties of High Burn-up Fuel

---

Annual Meeting of the European Working Group  
'Hot Laboratories & Remote Handling'  
ECN, Petten, The Netherlands  
May 14-15, 1996

T L Shaw, J C Carrol and R A Gomme



AEA Technology

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68  
69  
70  
71  
72  
73  
74  
75  
76  
77  
78  
79  
80  
81  
82  
83  
84  
85  
86  
87  
88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100



AEA Technology

## The Characterisation of the Thermal Properties of High Burn-up Fuel

BY

T L SHAW, J C CARROL and R A GOMME

### SUMMARY

This paper describes measurements of thermal diffusivity and specific heat performed on samples of irradiated  $\text{UO}_2$  ( $\sim 40$  GWd/tU), using the laser flash technique and differential scanning calorimetry technique, on experimental rigs specially adapted for in-cell use at Windscale.

Paper presented to the Annual Meeting of the European Working Group on "Hot Laboratories and Remote Handling", at ECN Petten, 14-15 May 1996.

AEA Technology plc  
Fuel Performance Group  
Windscale  
Cumbria  
CA20 1PF  
UK.

May 1996

S1



# Contents

1	Introduction
1	Thermal diffusivity
1	Method and data analysis
3	Specific heat
3	Equipment
3	Measurement procedure
4	Results
4	Thermal diffusivity
4	Specific heat
5	Discussion
6	Conclusion
7	References

- a “baseline” run with two empty crucibles (to establish a baseline);
- a “reference” run using a standard material with known properties (usually Sapphire);
- a “sample” run using the material of interest (for irradiated samples this will be the last stage to avoid contamination of the reference standards, which may be used again).

The temperature differential (expressed in micro-volts) between the two crucible thermocouples is measured during all three temperature scans and the data stored by the controlling computer. The sample specific heat,  $C_p^S$  (in J/g/K), is then given by the following expression

$$C_p^S = \frac{W_R}{W_S} \frac{\Delta V_S}{\Delta V_R} \cdot C_p^R \quad (2)$$

where:

$C_p^R$  is the specific heat of the reference standard (J/g/K)

$W_R$  is the weight of the standard (g)

$W_S$  is the weight of the sample (g)

$\Delta V_R$  is the voltage difference between the reference curve and the baseline ( $\mu V$ )

$\Delta V_S$  is the voltage difference between the sample curve and the baseline ( $\mu V$ )

## 4.0 Results

### 4.1 THERMAL DIFFUSIVITY

Figure 3 shows in graphical form, the data obtained from the thermal diffusivity measurement of a fragment of  $UO_2$  irradiated to 40 GWd/tU, over a temperature cycle 400–1400–400°C. For comparison purposes, data from a fragment of unirradiated  $UO_2$  is also shown.

### 4.2 SPECIFIC HEAT

A fragment of irradiated  $UO_2$  was obtained from an *adjacent position* to that from which the thermal diffusivity sample was derived, and in order to investigate the “specific heat” behaviour of this fragment the following measurement procedure was adopted:

- a pre-conditioning cycle comprising an isothermal hold at 800°C for half an hour to anneal out “low temperature” irradiation damage
- a temperature programme, as depicted in Figure 4, comprising a series of cycles to progressively higher temperatures with isothermal holds at the top of each up-ramp, each of a half hour duration, at 1000, 1200 and 1400°C. A ramp rate of 20°C/minute was used for the heating and cooling ramps.

## Introduction

In assessments of fuel performance, the fuel thermal conductivity is a key parameter, since for a given power rating it controls the operating fuel temperature, and hence influences other important aspects of fuel behaviour, eg fission gas release. Fuel thermal conductivity is known to degrade with burn-up, and as operators push to reduce costs by extending the fuel life to higher burn-ups, there is a need to ensure that such degradation will not compromise safety margins.

The direct measurement of thermal conductivity ( $k$ ) is not straightforward, although it may be derived from the measurement of thermal diffusivity ( $\alpha$ ), specific heat ( $C_p$ ) and density ( $\rho$ ), via the relationship:

$$k = \alpha \cdot \rho \cdot C_p$$

Irradiated ceramic fuel is extensively cracked due to large thermal stresses generated in-reactor, and the amount of cracking increases progressively with burn-up, with the result that sample preparation is difficult, and often only relatively small fragments can be obtained. However, although the typical size of samples available is relatively small, they are typically very active, which means that thermal properties measurements must be performed using equipment designed to operate in specially shielded facilities; both sample handling and equipment operation have to be carried out remotely.

At the Windscale Laboratory of AEA Technology, a laser flash rig for the measurement of thermal diffusivity has now been operating successfully in a shielded facility for a number of years. To complement this, a Netzsch DSC-404 differential scanning calorimeter has recently been installed in an adjacent shielded cell, for which a robotic system under operator control has been developed to enable precise crucible placement. This provides a unique capability of being able to perform *both* thermal diffusivity and specific heat measurements on irradiated fuel samples.

This paper describes the Windscale thermal property measurement capabilities, together with an example of such measurements on fuel irradiated to ~40 GWd/tU in a European BWR, using the laser flash method for thermal diffusivity and differential scanning calorimetry for specific heat.

## 2.0 Thermal Diffusivity

### 2.1 METHOD AND DATA ANALYSIS

A schematic diagram of the in-cell apparatus at Windscale is shown in Figure 1. A horizontal tantalum tube furnace is enclosed in a water cooled vacuum vessel which is evacuated to  $10^{-5}$ - $10^{-6}$  torr. The sample is mounted in a graphite holder, which is held on three parallel molybdenum rods positioned to be on the centre-line of the furnace. Temperature monitoring is achieved via two

tungsten-rhenium thermocouples entering opposite ends of the tube furnace. These two readings typically differ by no more than 5-10°C.

An incident pulse (of duration <1 ms) is provided by a 12 mm Nd-glass laser which is situated outside of the hot cell. This pulse passes through an aperture in the cell wall and into the vacuum chamber via a quartz window. The back surface of the sample is monitored by an In-Sb infra-red detector through a sapphire window and a calcium fluoride lens. The detector's field of view is restricted to the central 2 mm of the sample. A germanium filter is placed immediately before the detector to prevent the possibility of the detector being damaged by the direct 'shine through' of laser light.

The temperature response of the back surface is amplified and stored on a magnetic disc by a computer. The data storage sequence is triggered by the laser beam. The signal from the detector is monitored by a storage oscilloscope whose main function is to establish that thermal stability has been obtained, but also shows the temperature rise on the back surface of the sample.

For the idealised case of zero heat loss, the thermal diffusivity,  $\alpha$  (in m<sup>2</sup>/s), can be derived from the solution of the one-dimensional heat conduction equation, to give:

$$\alpha = \frac{0.13878l^2}{t_{0.5}}$$

where,  $l$  = the sample thickness (m)  
 $t_{0.5}$  = the time for the temperature of the sample back surface to reach half the maximum temperature (s)

Two of the standard analysis techniques commonly applied to measured thermal diffusivity data are:

- (i) the Cowan method<sup>(1)</sup>, which uses the trailing edge of the response curve to correct for losses from the sample front and back surfaces;
- (ii) the standard logarithmic method, applied to the rise of the response curve as specified by James<sup>(2)</sup> which utilises a Laplace Transform solution at short times, and does not use heat loss correction.

The Cowan method will be superior to the standard logarithmic technique at high temperatures where radiation heat loss will dominate. At low temperatures, where radial heat conduction (for small samples) contributes significantly to the total heat loss, the logarithmic method is more suitable (because at short times the effects of the radial heat losses are less important). At elevated temperatures, radiative heat losses from the sample cannot be neglected, and recent work at Windscale has led to a modified version of the standard logarithmic method to include a heat loss correction term, which was derived empirically from fits to idealised data over the temperature range of interest. The data reported here have been obtained via this "Windscale Corrected Logarithmic" method.

- an immediate repeat measurement using the same temperature programme.

The half hour holds at elevated temperature were aimed at approximating the times that were spent at those temperatures during the thermal diffusivity measurement sequence, in order that a comparison could be made between the two sets of measurements.

Figure 5(a) shows the effect of cycling the sample to progressively higher temperatures in the first set of heating cycles, while Figure 5(b) shows measurements on the same sample during the repeated temperature programme.

## 5.0 Discussion

Figure 3 shows two clearly distinctive features: (i) The depression of the diffusivity values of the irradiated material compared with the unirradiated; (ii) a hysteresis, or recovery effect, following heating to 1400°C.

The degradation compared with the unirradiated value is now a well known feature which arises from the presence of dissolved fission products, fission gas bubbles and radiation damage (eg vacancies, interstitials and dislocation loops). Metallic inclusions which also arise upon irradiation may be considered to act as “negative pores”, although the net effect of irradiation is clearly a degradation.

The recovery effect seen following annealing is believed ascribable to different processes at different temperatures, although the exact mechanisms are still to be elucidated. At temperatures of ~600-900°C, it is postulated that recovery occurs via the annealing out of irradiation damage, whereas at higher temperatures, recovery occurs as a result of fission products coming out of solution into bubbles, with subsequent coarsening leading to a reduction in the number of scattering centres and hence diffusivity recovery. Although such restructuring may be expected to occur in-reactor, where changes in bubble characteristics/populations will occur during temperature transients, such large recoveries are not expected since an equilibrium concentration of irradiation damage is maintained by the presence of a flux.

Figures 5(a) and (b) show the tendency for the specific heat of irradiated UO<sub>2</sub> to be slightly higher than that given by the simple algorithm in the ENIGMA fuel performance code, although to within the experimental uncertainties the differences are not considered significant. More importantly however, Figure 5(a) shows interesting changes in the specific heat during the progression of the heating cycle programme.

On the first up-ramp (to 1000°C) there is a steady increase in the specific heat up to ~800°C (at which temperature a pre-conditioning isothermal hold was performed), whereupon there is a marked decrease in its value - indicative of an exothermic process. On the second up-ramp (to 1200°C), a similar decrease is seen, but does not start until ~900°C. Such a temperature dependence of the change in behaviour is indicative of the recovery processes referred to above in the discussion of the thermal diffusivity data. On the third ramp (to 1400°C)

there is no evidence for this pattern of behaviour being repeated, which may indicate that the earlier half hour hold at 1200°C proved sufficient to complete the annealing process(es) seen at the lower temperatures. However, such a conclusion can only be tentative based on the data presented in Figure 5(a); above 1200°C a sharp increase in “apparent” specific heat is seen, but this is believed to be spurious and to result from a small amount of sample fragmentation (a small amount of particulate was found at the bottom of the crucible after the measurements).

This damage annealing hypothesis is further supported by Figure 5(b) showing a repeat temperature cycle performed after the sample has already been taken to a maximum temperature of 1400°C (with a half hour hold), and in which the features ascribed to annealing effects are not observed. Within the experimental scatter, a consistent behaviour is observed between each part of the temperature programme. The scatter is largely ascribable to the small sample size which was necessitated in this case due to the annular nature of the fuel being studied.

From Figure 5(a) it is clear that in a temperature up-ramp following an isothermal hold a decrease in “apparent” specific heat, due to exothermic process(es), is observed. The implication for in-reactor performance (e.g. in a transient) will depend upon how the “equilibrium” irradiation damage changes as a function of temperature, and also upon how fast the damage present can anneal (at that temperature) to reach a new equilibrium value.

As described in the introduction, measurements of thermal diffusivity and specific heat may be used (along with values of density) to determine values of thermal conductivity. The most meaningful determination of this parameter from the data presented, is from the ‘annealed’ values - ie data from the ‘down-ramp’ shown in Figure 3, and data from the second specific heat heating cycle in Figure 5(b).

Figure 6 plots the derived conductivity (based on a density value of 95% theoretical), and compares the values with those given by a UK recommendation. This figure would suggest that the recommendation for irradiated fuel is highly conservative, with the values derived from these measurements being some 30% higher (although still depressed compared with the recommendation for unirradiated fuel). However, as mentioned earlier, it is generally believed that the ‘fully annealed’ thermal diffusivity values are not comparable to in-reactor values, where the effects of an irradiation flux on microstructure must also be taken into account.

## 6.0 Conclusions

- Experimental facilities have been developed at AEA Technology Windscale for the measurement of the thermal diffusivity and the specific heat of irradiated fuel.
- Such measurements on BWR fuel irradiated to ~40 GWd/tU have been reported here and have been used to derive values of thermal conductivity.

- Thermal diffusivity values of the irradiated material are depressed compared with the unirradiated, while specific heat values are comparable with unirradiated values and perhaps very slightly enhanced.
- Both the diffusivity and specific heat data suggest there to be restructuring processes occurring during the heating cycles associated with the measurement techniques; the specific heat data suggest that these processes are exothermic. These have been attributed to the removal of irradiation damage and re-distribution of fission products, although the exact mechanisms are still to be elucidated.
- In a temperature ramp following an isothermal hold a decrease in “apparent” specific heat is observed. The implication for in-reactor performance will depend upon how the “equilibrium” irradiation damage changes as a function of temperature, and also upon how fast the damage present can anneal (at that temperature) to reach the new equilibrium value.
- Values of thermal conductivity have been derived from these measurements, and are considered relevant to the fully annealed condition. These values are higher than a recommendation for irradiated fuel, although it is concluded that the annealed values are not directly appropriate for modelling the in-reactor situation, where the effects of a flux also need to be considered.

## References

1. COWAN R. D. Pulse method of measuring thermal diffusivity at high temperatures. *J Appl Phys* 34 926 (1963).
2. JAMES H. M. Some extensions of the flash method for measuring thermal diffusivity. *J Appl Phys* 4666 (1980).
3. KAISERBERGER E, JANOSCHEK J and WASSMER E. A heat flux DSC for enthalpy and specific heat determinations to 1700K. *Thermochimica Acta* 148 499 (1989).

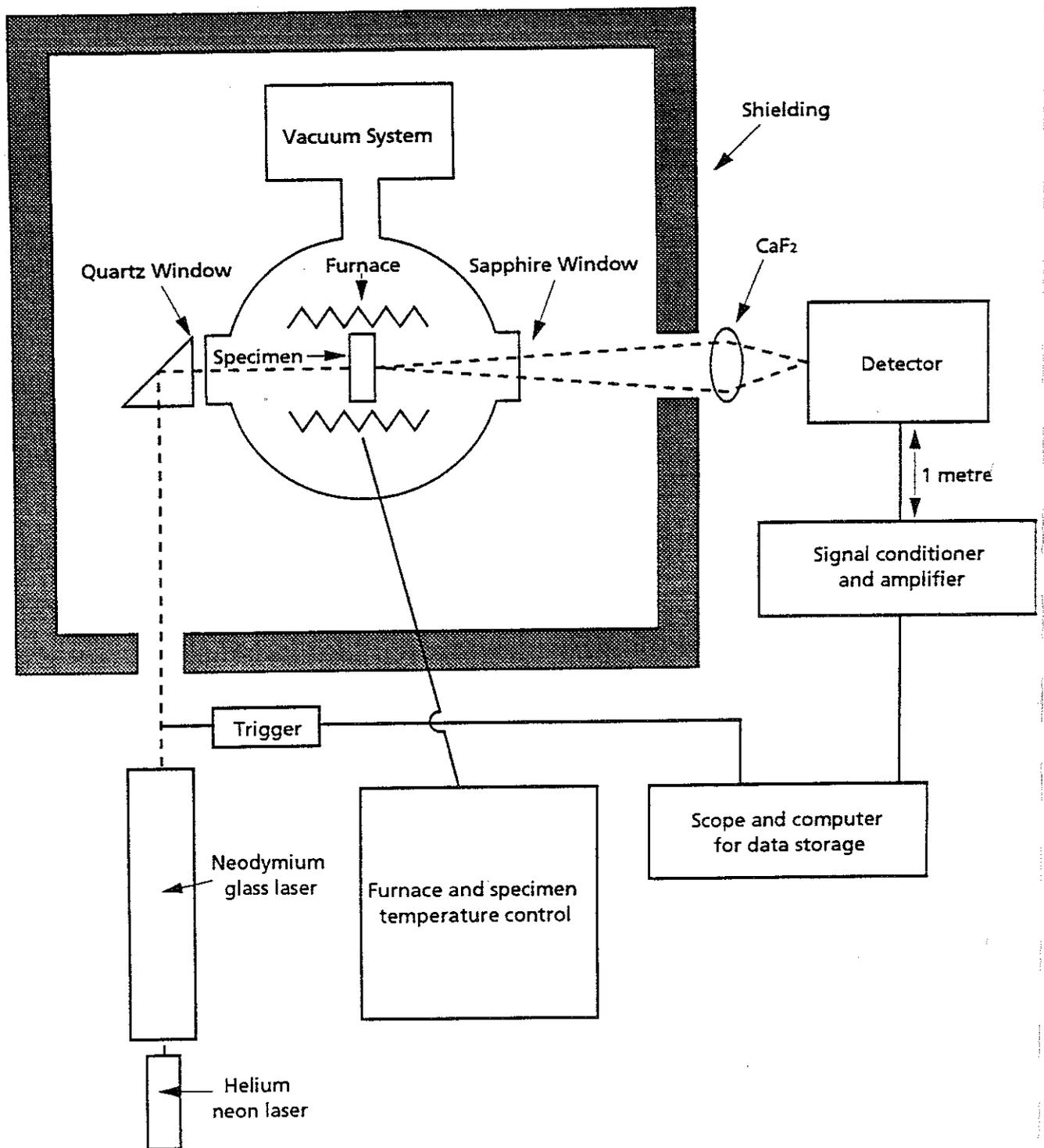
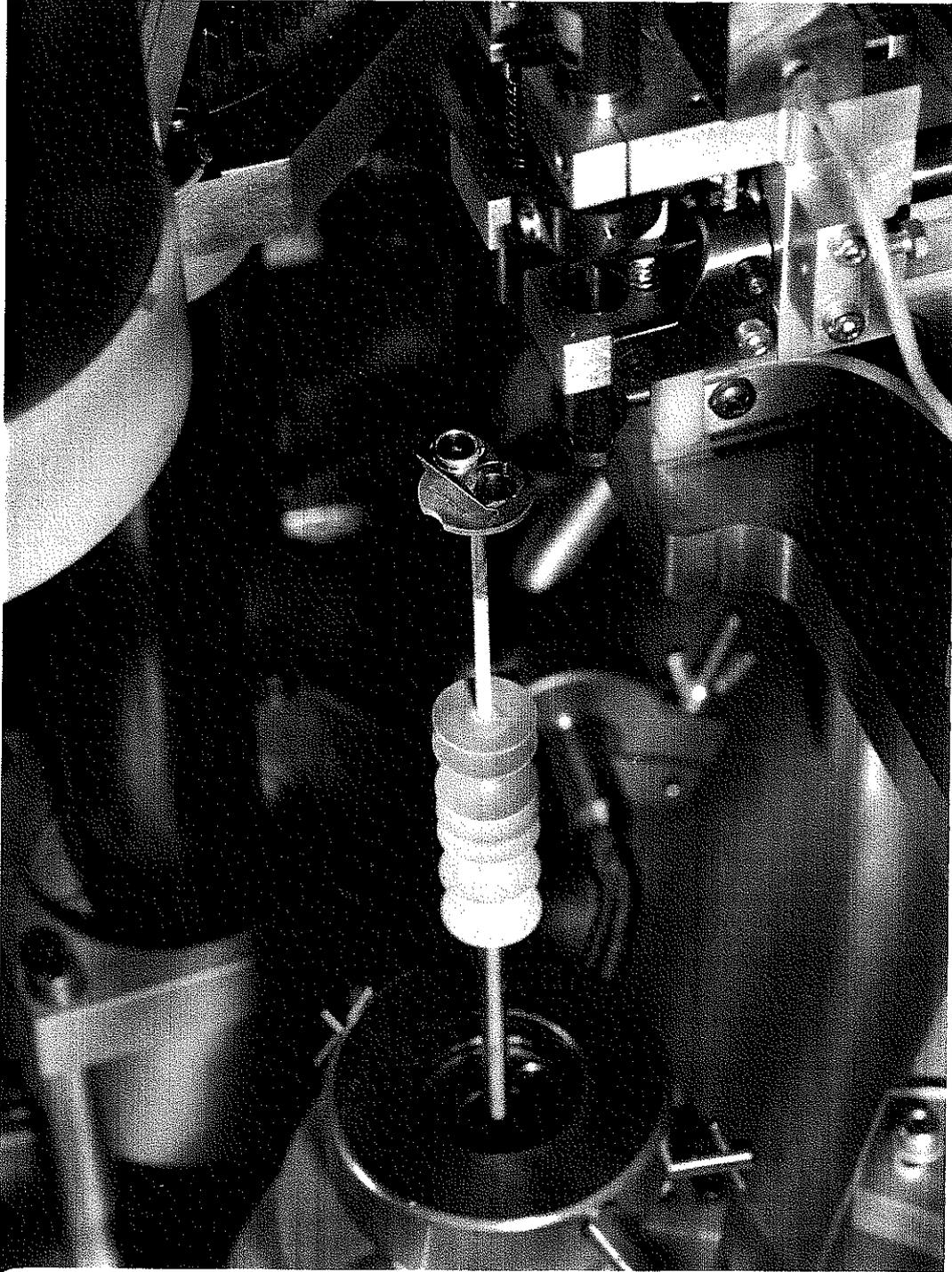


FIGURE 1 Schematic Diagram of Thermal Diffusivity Measurement Apparatus



**FIGURE 2** Specific heat measurement equipment - showing measurement stem, pick-up head and robot

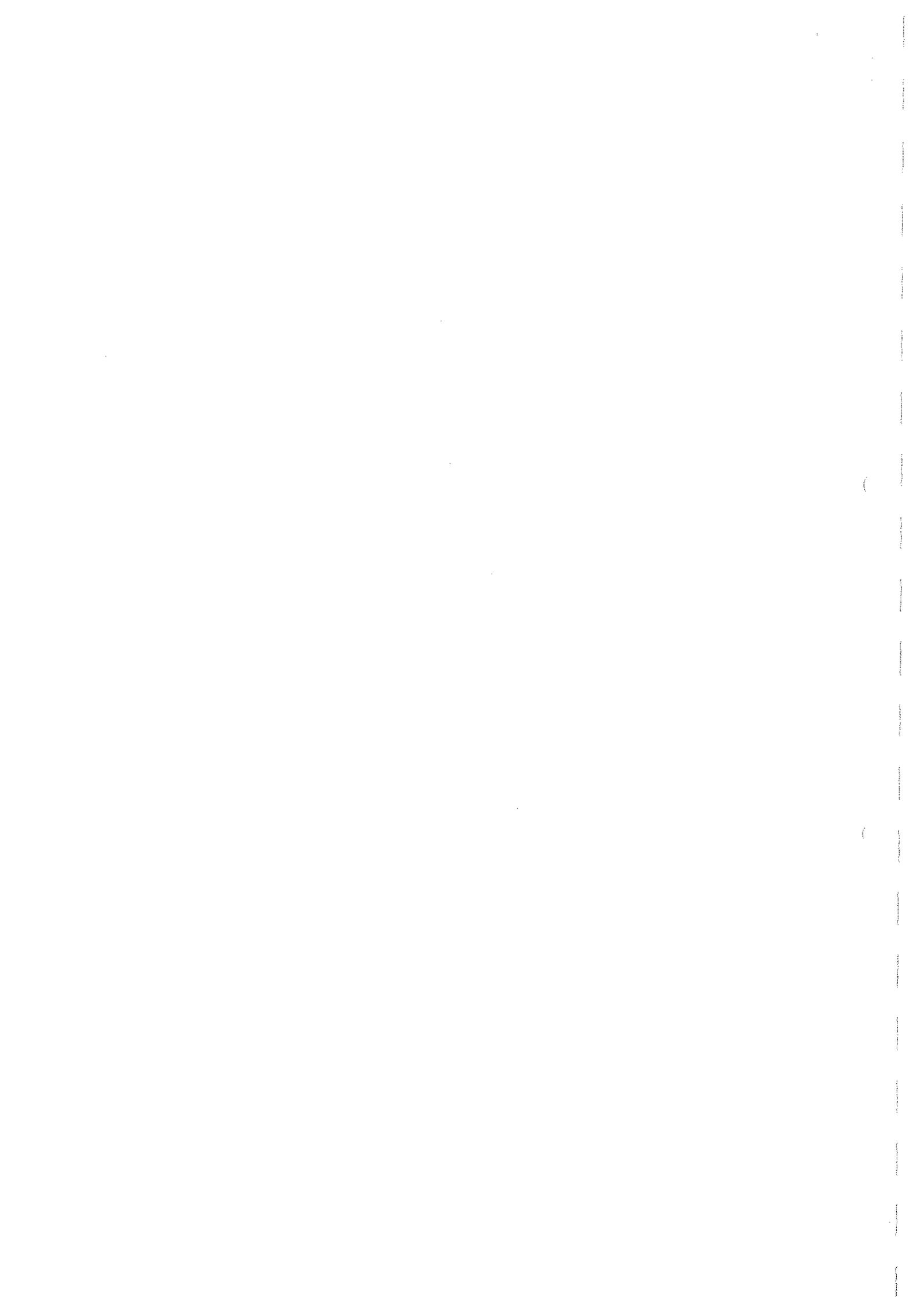


Figure 3. Thermal diffusivity measurements on unirradiated and irradiated Urania.

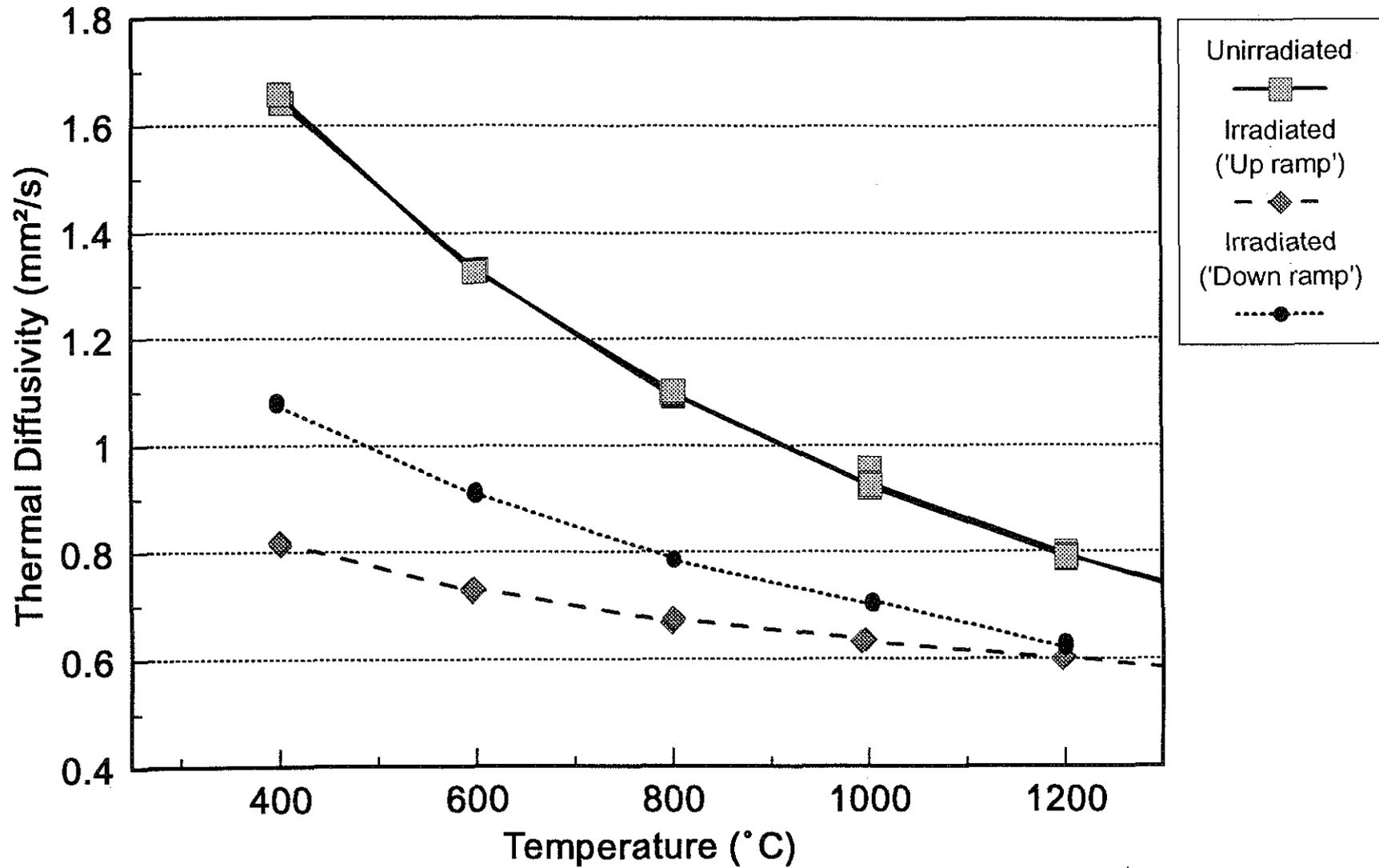


Figure 4. Representation of temperature programme with ramp rates of  $\pm 20^{\circ}\text{C}/\text{min}$  and isothermal hold durations of 30 minutes

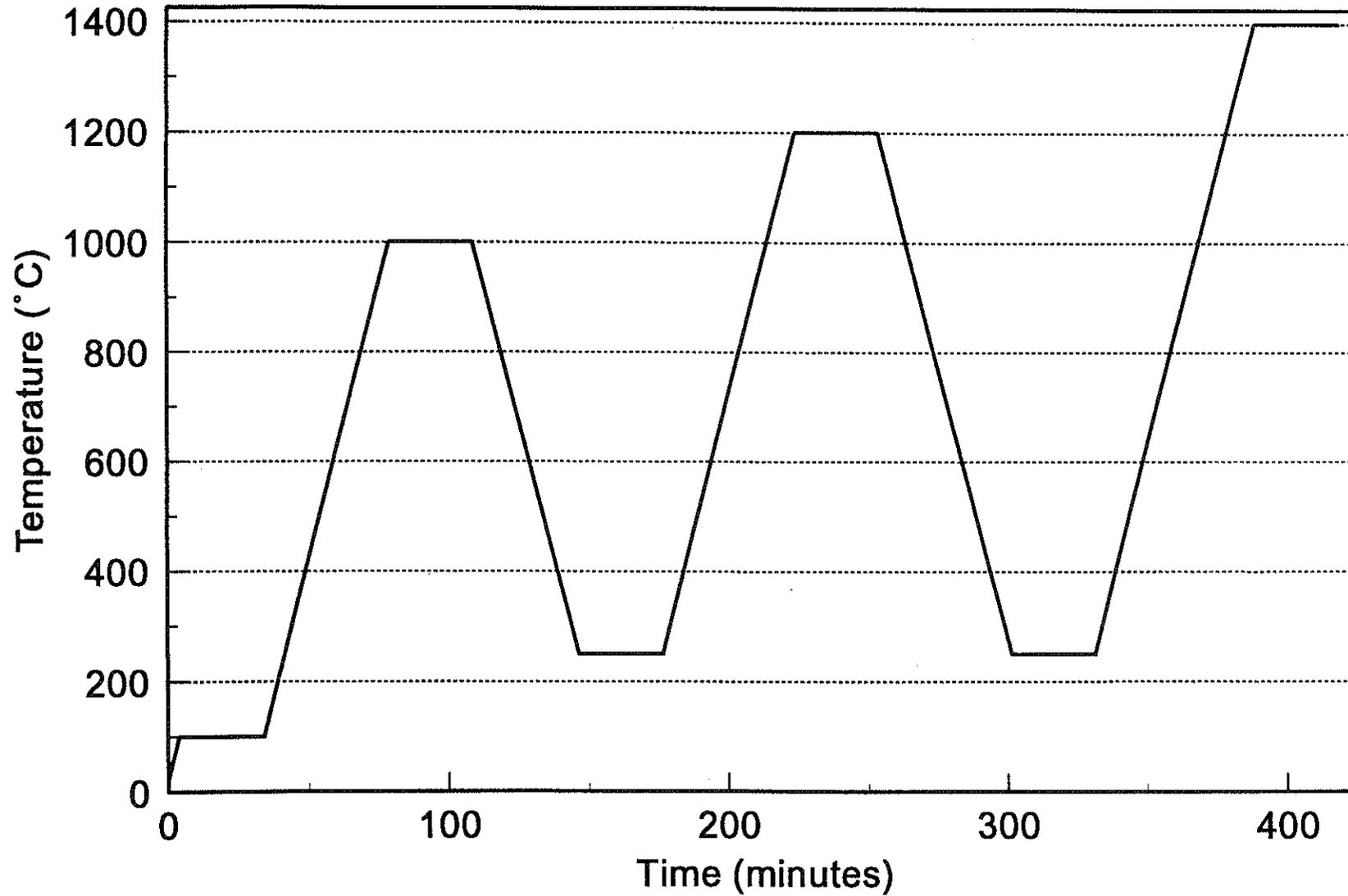


Figure 5. Specific heat determinations for irradiated Urania for (a) the initial temperature programme, T-1, and (b) the same programme repeated, T-2.

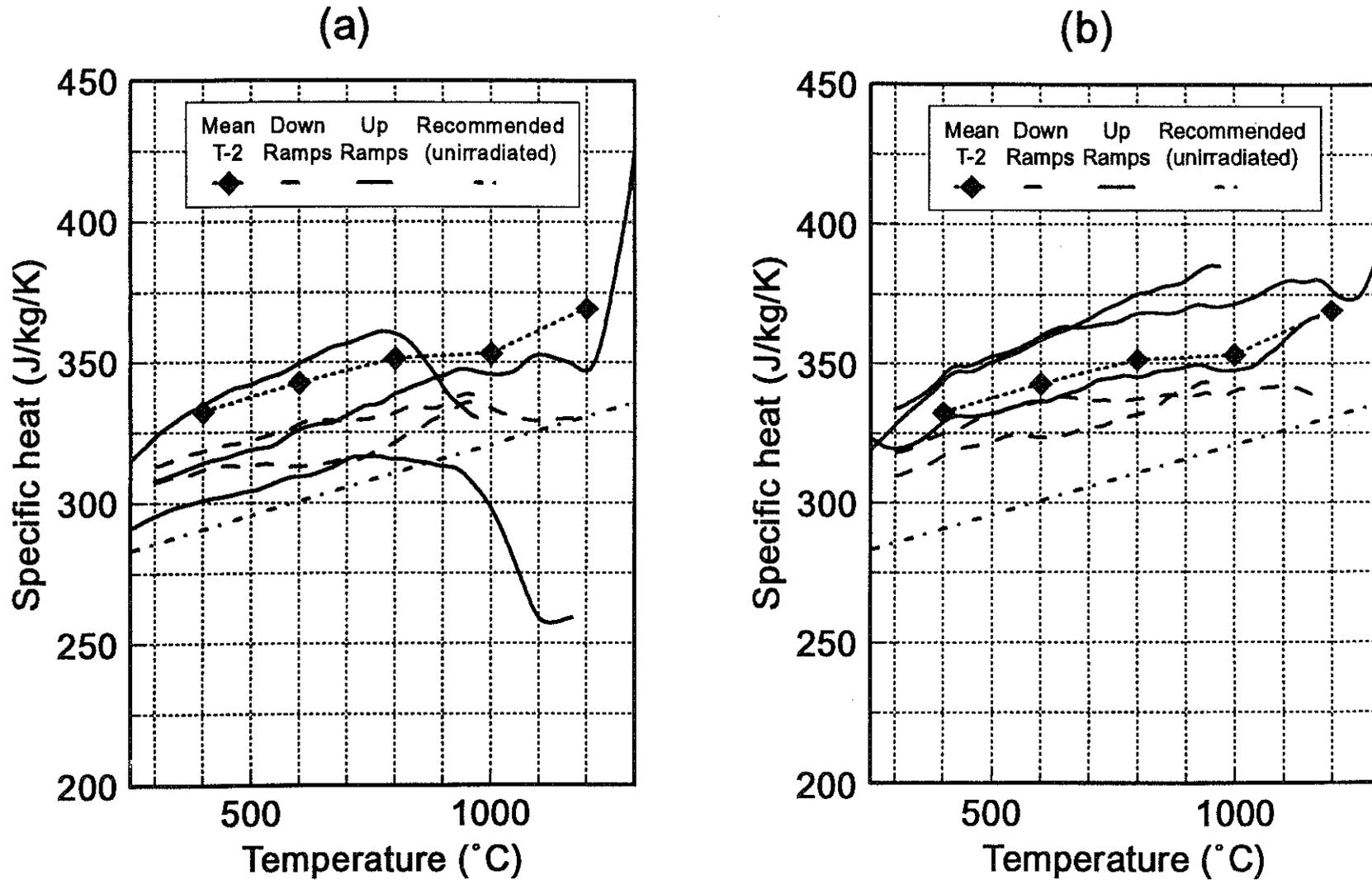


Figure 6. Comparison of derived thermal conductivity with UK recommendation.

