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DILATOMETRIC MEASUREMENT OF MELTING BEHAVIOUR OF METAL ALLOYS

(PROJECT IMP5)

by

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Summary

The use of double piston cells and conventional dilatometry for the determination of the melting and liquid thermal expansion characteristics of metals and alloys has been evaluated. The technique has been successfully applied to aluminium alloys using a boron nitride cell, and has permitted the density as a function of temperature to be determined through the so-called "mushy" zone and as a liquid. Tests on low-melting alloys were less successful due to leakage from the dies, and tests on high-melting alloys have not been completed during the time-span of this project due to difficulties of cost-effective die fabrication in appropriate materials.

It has been established that for successful operation a number of criteria have to be satisfied. The metal should not interact with, and preferably should not wet the cell. The pistons in the cell must slide smoothly, but the cell wall/piston gap must be as small as possible consistent with smooth, substantially friction-free sliding in order to avoid leakage. The starting metal dimensions must permit a thermal expansion mismatch allowance to the melting point to avoid cell fracture, but must not be excessive so that there is a large apparent contraction on melting.

It should be noted that because the pressure that can be applied to the pistons is limited to avoid leakage, the technique does not give the full melting curve, but only over the temperature range above that at which a rigid dendritic network exists. Below this temperature, the minimal force applied to the cell to avoid leakage is insufficient to crush the network, and residual liquid is drawn away from the surface of the test-piece, or the test-piece cavitates or collapses, and piston movement does not reflect the true volume changes.

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Contents

	Symbols	4
1.	INTRODUCTION	5
2.	THEORY OF OPERATION OF THE DOUBLE PISTON CELL	5
2.1	Assumptions	5
2.2	Symbols	6
2.3	Solid metal alloy	6
2.4	Melting with no melting range	6
2.5	Liquid metal expansion	8
2.6	Presence of a melting range	9
3.	EXPERIMENTAL	9
3.1	Dilatometer	9
3.2	Test cells	10
3.3	Data processing	10
3.4	Test alloys	11
3.5	Test procedure	11
4.	RESULTS	12
4.1	Tin and tin/indium alloy in Macor cell	12
4.2	Aluminium alloy in Macor cell	13
4.3	Pure aluminium in boron nitride cell	14
4.4	Aluminium/silicon alloy 1 (LM25) in boron nitride cell	15
4.5	Aluminium-silicon-copper alloys 2 and 3 in boron nitride cell	16
4.6	Alumina dies for higher temperature work	16
5	DISCUSSION	18
5.1	Cell behaviour	18
5.2	Behaviour of metal alloys in the cell	18
5.3	Accuracy analysis	19
6.	CONCLUSIONS	20
	Acknowledgements	20
	References	21
	Figures	22

Symbols

α_c	Linear thermal expansion coefficient of the cell material
α_{ms}	Linear thermal expansion coefficient of solid metal alloy
β_{ml}	Volumetric expansion coefficient of liquid metal alloy
ρ_{ms}	Density of solid metal
ρ_{ml}	Density of melting/liquid metal
$\Delta\rho$	Density change in metal on melting
l_{ml}	Apparent length of liquid metal in cell
l_{ms}	Apparent length of test-piece between pistons
Δl_ρ	Length change of sample in cell resulting from density change on melting
Δl_{ms}	Length change of solid metal
Δl_m	Length change on melting resulting from filling the cell
L	Total length of test-piece plus cell pistons
ΔL_{tot}	Total length change measured on melting
ΔL	Length change of test-piece plus cell pistons
m_m	Mass of metal sample
R_c	Radius of the cell as a function of temperature
R_{ms}	Radius of the solid metal test-piece as a function of temperature
T_S	Melting point of alloy, solidus
T_L	Melting point of alloy, liquidus
ΔT	Temperature change from a reference temperature, normally room temperature
V_{mm}	Volume of metal in molten condition
V_{ms}	Volume of solid metal at any temperature T below the solidus
ΔV_ρ	Volume change of metal on melting
ΔV_m	Volume mismatch between cell and sample at onset of melting
x_1, x_2	Lengths of the two pistons at start of test
$\Delta x_1, \Delta x_2$	Length changes of two pistons at temperature change ΔT from room temperature

1. INTRODUCTION

The behaviour of metal alloys during cooling is of concern in optimising the design of casting procedures. The rate at which heat is released in a casting depends on the solidification curve, and the rate at which it can be removed from the casting is determined by the thermal transport behaviour between the casting and the mould, and hence on any gap developing between the casting and the mould. Knowledge of the density of the alloy during melting/solidification is thus of considerable importance to the casting industry.

Techniques such as differential scanning calorimetry can be used to identify the heat content as a function of temperature during cooling, and from such data it is possible to estimate the state of solidification as a function of temperature, i.e. the volume fraction of liquid in the alloy a function of temperature between liquidus and solidus. However, in practice additional factors are involved. As a metal alloy solidifies a dendritic framework of the highest melting component develops. When these dendrites impinge, a rigid framework can be set up. Further solidification results in restriction of shrinkage, and the remaining liquid phase tends to be sucked inside. Alternatively, the casting may cavitate if liquid flow cannot be maintained. Thus the actual behaviour of an alloy cannot necessarily be predicted from thermodynamic considerations.

One possible route to identifying the role of dendrite impingement is to study the behaviour using a dilatometric method to follow the apparent volume of the solidifying metal [1, 4]. To do this the molten alloy must be contained within a rigid cell the dimensions of which as a function of temperature must be known. The cell is typically a cylinder with two protruding pistons. In addition, there should be minimal leakage of the cell, and the metal alloy should not react with the cell lining and prevent the cell from operating effectively.

This report covers a mathematical analysis of behaviour of such cells, experimental studies of the use of cells, and identification of the limits of performance and accuracy.

2. THEORY OF OPERATION OF THE DOUBLE PISTON CELL

2.1 Assumptions

In order to process the thermal expansion data derived from the dilatometer it is essential to develop the baseline theory for the operation of the double piston cell. For this purpose it is necessary to make a number of assumptions, some of which may not be realisable in practice. the assumptions are as follows:

1. The cell is frictionless, and follows the thermal expansion/contraction of the test material between the pistons.
2. The cell comprises of a material which behaves reproducibly in its thermal expansion/contraction behaviour with no net changes over a cycle.
3. On heating, test material remains effectively a solid until it reaches a temperature at which the piston pressure causes the structure to collapse, completely filling the volume of the cylinder, and similarly on cooling, the changes in volume of the liquid and solidifying alloy are followed until sufficient strength is developed to bear the piston force. It is also assumed that there is no plastic deformation due to push-rod pressure prior to collapse by melting.

4. There is no leakage of metal out of the cell between cylinder and pistons, i.e. the mass of the metal alloy is conserved.
5. Oxidation of the alloy and interaction or adhesion effects between the alloy and the cell walls are negligible.

Assuming that the behaviour on heating or cooling is similar, and can be analysed in a similar fashion, three regimes of behaviour need to be established: solid expansion, melting and liquid expansion. The relationship between melting and liquid behaviour has to be determined in terms of the parameters measurable at room temperature and the linear displacement recorded by the cell as a function of temperature. This is done below assuming first that there is no melting temperature range, and then adding the effects of a melting range.

2.2 Symbols

The symbols employed in the analysis are given before the Introduction (p4).

2.3 Solid metal alloy

Consider a test-piece in a cell. The response of the cell as recorded by the dilatometer, ΔL is the sum of the expansions of the pistons, Δx_1 , Δx_2 , and of the solid test-piece, Δl_{ms} :

$$\Delta L = \Delta x_1 + \Delta x_2 + \Delta l_{ms} \quad (1)$$

Substituting using the expansion coefficients of the respective materials and the temperature range ΔT from room temperature:

$$\Delta L = (x_1 + x_2)\alpha_c\Delta T + l_{ms}\alpha_{ms}\Delta T \quad (2)$$

from which the expansion coefficient of the metal sample can be derived by rearranging:

$$\alpha_{ms}\Delta T = \frac{\Delta L}{l_{ms}} - \frac{(x_1 + x_2)\alpha_c\Delta T}{l_{ms}} \quad (3)$$

This equation needs to be used to eliminate the expansion effects of the cell.

2.4 Melting with no melting range

Since the volume of the solid metal sample at the melting point does not necessarily equal the volume of the cell, there could be a mismatch which results in a drop in apparent length as the cell fills completely on melting. This needs to be taken into account.

The volume of the metal sample at the "melting point" (i.e. the point at which the test-piece appears to become liquid and begins to collapse to the shape of the die) is:

$$V_{ms}(T_S) = V_{ms}(0) (1 + 3\alpha_{ms}T_S) \quad (4)$$

referenced to room temperature $T = 0$. The radius of the metal sample at this point (assuming no prior plastic deformation) is:

$$R_{ms}(T_S) = R_{ms}(0) (1 + \alpha_{ms} T_S) \quad (5)$$

The volume of the metal sample at melting is thus given by:

$$V_{ms}(T_S) = \pi R_{ms}^2(T_S) l_{ms} = \pi R_{ms}^2(0) l_{ms}(0) (1 + 3\alpha_{ms} T_S) \quad (6)$$

The radius of the cell at melting is:

$$R_c(T_S) = R_c(0) (1 + \alpha_c T_S) \quad (7)$$

and the volume of the cell at T_S is thus:

$$V_c(T_S) = \pi R_c^2(0) l_{ms} (1 + 2\alpha_c T_S) (1 + \alpha_{ms} T_S) \quad (8)$$

The volume difference between the metal sample and the cell at the point of melting is thus:

$$\Delta V_m = V_c(T_S) - V_{ms}(T_S) \\ \pi (1 + \alpha_{ms} T_S) l_{ms}(0) [R_c^2(0) (1 + 2\alpha_c T_S) - R_{ms}^2(0) (1 + 2\alpha_{ms} T_S)] \quad (9)$$

It is clear from this expression that to fill the geometry of the cell, the metal sample should ideally exactly match the cell at the melting point, which can be achieved by setting the term in parenthesis to zero, i.e. by achieving:

$$R_c(0) (1 + \alpha_c T_S) = R_{ms}(0) (1 + \alpha_{ms} T_S) \quad (10)$$

To do this at the outset of the test requires prior knowledge of the expansion behaviour of both cell and metal alloy, which would have to be determined separately, even though that of the metal could be deduced from the cell test alone. Normally, the test would be arranged so that the solid metal did not expand sufficiently to stress the cell wall before melting, so that a small drop in length is likely.

If there is no change in specific volume of the metal on melting, melting to fill the cell would result in a change in length, Δl_m , where:

$$\Delta V_m = - \Delta l_m \pi R_c^2(T_S) \quad (11)$$

Substituting into equation (9) gives:

$$\Delta l_m = - l_{ms}(0) (1 + \alpha_{ms} T_S) \left[1 - \frac{R_{ms}^2(0) (1 + 2\alpha_{ms} T_S)}{R_c^2(0) (1 + 2\alpha_c T_S)} \right] \quad (12)$$

The general case is where the metal dimensions are smaller than the ceramic dimensions at the melting point, resulting in a net cell length shrinkage on melting.

If additionally the density of the molten metal changes by $\Delta \rho$ at the melting point a correction needs to be made. Normally $\Delta \rho$ is negative, so that the volume increases. The density of the solid metal at the melting point is given by:

$$\rho_{ms}(T_S) = \frac{m_m}{\pi R_{ms}^2(0) l_{ms}(0) (1 + 3\alpha_{ms}T_S)} \quad (13)$$

On melting, the increase in volume, ΔV_ρ , is related to the change in density by:

$$\Delta V_\rho + \frac{m_m}{\rho_{ms}(T_S)} = \frac{m_m}{\rho_{ms}(T_S) + \Delta \rho} \quad (14)$$

whence:

$$\Delta V_\rho = m_m \left(\frac{1}{\rho + \Delta \rho} - \frac{1}{\rho} \right) = m_m \left(\frac{-\Delta \rho}{\rho(\rho + \Delta \rho)} \right) \quad (15)$$

i.e. is positive if $\Delta \rho$ is negative. The apparent change in length of the test-piece resulting from this is given by:

$$\Delta l_\rho = \frac{\Delta V_\rho}{\pi R_c^2(T_L)} = \frac{m_m}{\pi R_c^2(T_L)} \left(\frac{-\Delta \rho}{\rho(\rho + \Delta \rho)} \right) \quad (16)$$

assuming that the cell remains filled during this process. The net change on melting is thus due the sum of equations 16 and 12. To calculate $\Delta \rho$, equation 16 can be rearranged:

$$\Delta \rho = \frac{\rho^2}{\rho + \frac{m_m}{\pi R_c^2(T_S) \Delta l_\rho}} \quad (17)$$

where $\rho = \rho_{ms}(T_S)$. If the total measured change is Δl_{tot} , Δl_ρ can be calculated as:

$$\Delta l_\rho = \Delta l_{tot} - \Delta l_m \quad (18)$$

where Δl_m can be calculated from equation 12. The solid density at the melting point, $\rho_{ms}(T_S)$, can be derived from:

$$\rho_{ms}(T_L) = \frac{\rho_{ms}(0)}{(1 + 3\alpha_{ms}T_L)} = \frac{m_m}{\pi R_{ms}^2(0) l_{ms}(0) (1 + 3\alpha_{ms}T_L)} \quad (19)$$

2.5 Liquid metal expansion

The most convenient way of dealing with liquid metal expansion is to reference it to the liquidus temperature T_L . Assuming that the volume of liquid fills the cell diameter, and that there is no leakage, the volume of the test sample as a function of temperature is given by:

$$V_{ml}(T) = V_{ml}(T_L) [1 + \beta_{ml} (T - T_L)] \quad (20)$$

Substituting the volumes by the cell radius and length yields:

$$\beta_{ml}(T - T_L) = \frac{R_c^2(T) l_{ml}(T)}{R_c^2(T_L) l_{ml}(T_L)} - 1$$

$$(1 + 2\alpha_c(T - T_L)) \left(\frac{l_{ml}(T)}{l_{ml}(T_L)} \right) - 1 \quad (21)$$

where:

$$l_{ml}(T) = L(T) - (x_1 + x_2)(1 + \alpha_c T) \quad (22)$$

The density of the liquid metal is given by:

$$\rho_{ml}(T) = \frac{m_m}{V_{ml}} = \frac{m_m}{V_{ml}(T_L) [1 + \beta_{ml}(T - T_L)]} \quad (23)$$

where β_{ml} can be obtained from equation 21, and:

$$V_{ml}(T_L) = \pi R_c^2(0)(1 + 2\alpha_c T_L)[L(T_L) - (x_1 + x_2)(1 + \alpha_c T_L)] \quad (24)$$

Alternatively, β_{ml} can be obtained by curvefitting the data from equation 23.

2.6 Presence of a melting range

If the metal has a melting range between an effective solidus T_S and a liquidus T_L , consider the true volume occupied at temperature $T_S < T < T_L$:

$$V_{mm}(T) = \frac{m_m}{\rho(T)} \quad (25)$$

whence:

$$\rho_{ml}(T) = \frac{m_m}{\pi R_c^2(0) (1 + 2\alpha_c T) [L(T) - (x_1 + x_2)(1 + \alpha_c T)]} \quad (26)$$

It is interesting to note that the density of the metal in this temperature range, and indeed above the liquidus (equation 23) is independent of the solid expansion coefficient of the metal and of any size mismatch on melting, and requires only that the absolute length of the cell is known. Since this is normally what is measured by the dilatometer, in principle the density determination can be as accurate as the determinations of the cell radius and its expansion coefficient permit.

3. EXPERIMENTAL

3.1 Dilatometer

The dilatometer used for this work was a conventional horizontal push-rod dilatometer manufactured by Linseis GmbH, Selb, Germany, but with modified test-piece holder and furnace. The test-piece holder and push-rod are made from transparent fused silica.

Temperature of the test-piece is measured using a Type R (Pt/13%Rh-Pt) thermocouple in contact with the external cell wall and shielded from the furnace by a small piece of fibre insulation. Push-rod displacement is measured with a sensitive linear displacement transducer. The outputs from the thermocouple and transducer are logged at typically 2 minute intervals using a datalogger.

The apparatus is calibrated for thermal expansion measurement in the following way. The silica test-piece holder is removed, and replaced by a drum micrometer which is used to move the push-rod prescribed amounts. In this way the absolute sensitivity of the transducer may be determined. The apparatus is reassembled and run over the required temperature range with a fused silica test-piece of the same material as the push-rod, and any shift of the baseline output, corresponding to differential temperature distributions in the specimen support and push-rod, is determined. This is used to correct the output from testing an unknown. The correction for the expansion coefficient of the apparatus itself may be determined by inserting a certified reference test-piece, normally SRM 739, Fused Silica from the National Institute for Standards and Technology, USA. The test is performed in accordance with NPL procedure QPDMM/B/119 (low temperature) or QPDMM/B/120 (high temperature), which are in line with EN 821-1.

The overall accuracy of the measurement is controlled by the mechanical stability of a rigid specimen in the apparatus. Assuming complete stability, the measurement accuracy is considered to be approximately $\pm 0.2 \times 10^{-6} \text{ K}^{-1}$ over a 100 K temperature range.

Test cells

Test cells were designed to fit into the test-piece support, and comprised a tubular body about 18 mm in length, 6 mm bore and 2 mm wall thickness. The two pistons were about 6 mm long and 6 mm diameter. They were machined to have just sufficient clearance (about 0.01 mm to 0.02 mm) in the cylinder to permit free sliding movement. The cells were first made in Macor® (machinable glass-ceramic, Corning Glass Works), and later in hot-pressed boron nitride and alumina.

The expansion behaviour of the cell materials was measured directly in the dilatometer to above the maximum likely test temperature (Figures 1 and 2). The data from these tests were transferred to an Excel spreadsheet and a polynomial fit for both heating and cooling parts of the curve prepared (Figures 3 and 4).

Data processing

The logged data are processed first as though the test-piece is a rigid conventional test material. This is essential, because it is necessary to correct for the apparatus baseline shift and thermal expansion. The output from this gives the expansion in parts per million from zero at the start of the test.

The second part of the calculation prepared specially for the present work is to transfer the corrected data to an Excel spreadsheet in which the following steps are undertaken.

1. Insert test-piece starting parameters, length, diameter, mass.
2. Insert cell bore, piston lengths and total length of test-piece in the cell.

3. Insert test data comprising data pairs of logged temperature and expansion in parts per million.
4. For each temperature, compute the true length of the test-piece plus pistons $L(T)$ throughout the measurement cycle.
5. Using a polynomial fit for the thermal expansion behaviour of the cell material α_c , for each temperature correct the length data for the piston expansion and deduce the true alloy sample length.
6. Identify the temperature points corresponding with the onset and completion of melting from the expansion trends.
7. For temperature below the onset of apparent melting, calculate the effective solid expansion coefficient and the solid density.
8. For temperatures above the onset of apparent melting, calculate the partially or fully molten density.
9. Prepare plots of each section of density data comprising solid, melting plus liquid and liquid only.
10. For the liquid-only plot, use the Excel linear regression program to calculate the slope of the liquid expansion data set, from which the volumetric coefficient of expansion may be determined.

3.4 Test alloys

Cylindrical test-pieces were prepared mostly by machining, but in the case of low-melting alloys, also by melting and casting into a graphite die. Care was taken to prepare flat ends on the test-piece. The diameter of the test-piece was prepared to be less than that of the cell bore by an amount sufficient to accommodate the differential thermal expansion between alloy and cell to the melting point. Since it was judged that this did not need to be done particularly accurately, the expansion behaviour for the metal was taken from tables and extrapolated to the melting point.

The following test materials have been examined:

Tin

Tin/indium alloy (approximately 80:20 by weight)

Aluminium

Aluminium/silicon alloy 1 (LM25)

Aluminium/silicon/copper alloys A and B (proprietary)

3.5 Test procedure

The cell internal diameter was measured at both ends to the nearest 0.01 mm using a travelling microscope, and the piston lengths and diameters were measured to the nearest 0.001 mm using a vernier micrometer.

The machined metal alloy test-piece was cleaned and weighed to the nearest 0.01 mg. The

diameter and length were measured at several positions and the averages taken. The test-piece was placed in the cell with the pistons protruding about 1 mm each end, and the total cell length checked.

The cell was then placed in the dilatometer, and the measurement procedure commenced. The maximum temperature was set to be typically 50 °C above the suspected liquidus, and the heating rate to be 1 or 2 °C/min. The complete thermal cycle was recorded.

Depending on the outcome of the test, either the test system was demounted and the alloy sample inspected, or a further cycle was made immediately.

4. RESULTS

4.1 Tin and tin/indium alloy in Macor cell

The first tests were undertaken on tin and an indium/tin alloy which are simple low-temperature systems in which very little reaction between the cell and the metal or alloy is expected. The tests are summarised in Table 1.

After initial problems with leakage, an attempt was made to build up the diameter of the pistons using a graphite spray, but this was only partly successful, and leaks still occurred (Figures 7 and 8). It was clear from the thermal expansion data successfully extracted that the pistons were not moving freely, and that as the liquid metal expanded, it was forced down the gap. Only short temperature intervals revealed the true behaviour. On cooling, however, the results were more consistent and in line with expectations. However, on removal from the cell, the test-pieces were found to contain voids, or no longer to have cylindrical geometry (Figure), suggesting that there was a "feeding" problem, probably because the parts in contact with the cell walls and piston solidified first, and the solidification shrinkage of the central region resulted in some collapse. In view of the loss of metal, detailed estimates of density and liquid expansion coefficient were not conducted.

The behaviour of the tin test-pieces was consistent with a single melting point at 225 °C as expected. On cooling after melting, there was some undercooling to 210 °C noted, with sudden release of the heat of solidification causing the externally measured cell temperature to rise briefly (Figure 5). This is broadly in line with expectations.

The behaviour of the In/Sb alloy appeared to be better controlled. For the first trial cast, the overall cell thermal expansion behaviour in the first cycle showed an apparently progressively increasing contraction above about 145 °C, followed by an expansion above 175 °C, and then a much lower expansion above 190 °C up to 240 °C (Figure 6 (left)). It is presumed from this behaviour that the liquidus is 190 °C, and the solidus is probably at about 145 °C. The cooling curve in the liquid state between 240 °C and 190 °C is rather steeper than the heating curve, suggesting that some leakage occurred during heating. A steep shrinkage then set in at 190 °C, levelling off at about 175 °C. The run showed no discontinuities. The second thermal cycle on this test-piece showed linear behaviour to about 180 °C, followed by a slight expansion and completion of melting at 190 °C (Figure 6 (right)). The maximum temperature employed was 300 °C, and again there was a difference between the heating and cooling curves in the liquid state, which can only be ascribed to progressive leakage during heating. The shape of the cooling curve below 190 °C was the same as in the first cycle. The difference between the heating curves of the first and second cycles was probably due to filling the gap between the test metal cylinder and the cell in the first cycle, while in the

second cycle, the cylinder dimensions have been redefined by melting and cooling. On removal from the cell, the test-piece was found to have good geometry with a fine scale surface dendritic microstructure and no cavitational voidage. The roughness of the surface suggested some uniformly distributed suction of surface liquid into the bulk of the test-piece.

Table 1 - Tests using tin and tin/indium alloy

Run ref.	Metal alloy	Cell material	Piston coating	Outcome
E4584	Sn	Macor	None	Two cycles. In first, large drop in length on melting at 225 °C. Small bead of metal expelled. Slight voiding seen on removal. In second, melt drop seen, followed by stable length as liquid, but cooling curve different. Undercooled to 210 °C before solidifying. (Figure 5 (left))
E4585	Sn	Macor	Graphite	Single cycle. Same test-piece as E4584. Similar behaviour as second cycle of E4584. Voiding noted. (Figure 5 (right), 7)
E4586	Sn	Macor	Graphite	Single cycle. Large amount of leakage. Results ignored. (Figure 8 (left))
E4588	Sn	Macor	Graphite	Three cycles. Large drop on melting in each cycle. Some leakage on each cycle. Results ignored.
E4590	Sn/In	Macor	Graphite	Two cycles. In first cycle above 140 °C specimen progressively collapsed, but expanded above 175 °C. Liquidus 190 °C. Second cycle remained solid to 180 °C, liquidus 190 °C. Liquid expansion on heating not the same as on cooling. Some undercooling on second cycle but not first. Cell leaked slightly; some metal between cell and piston. (Figure 6, 8 (right))
E4590	Sn/In	Macor	Graphite	Three cycles. Large length drop on melting. Checked after first and third cycles only. Some leakage in all cycles.

A repeat experiment was performed on a second casting (Figure 8 (right)), but unfortunately, this sample leaked more extensively and was abandoned.

4.2 Aluminium alloy in Macor cell

The next experiment was an attempt to use the Macor cell for a typical aluminium alloy, Dural. It was clear from the thermal expansion trace that the pistons were not moving smoothly, and although melting was detected above about 650 °C, the recorded displacements were jerky and not usable, and some leakage was discovered. On removal of the cell from the apparatus it was found that the aluminium had reacted with Macor, bonding to it. The

test-piece could be removed only by destroying the cell. In cross-section, the Macor showed an extensive reaction zone, and fragments of Macor were strongly adherent to the aluminium (Figure 9 (left)).

4.3 Pure aluminium in boron nitride cell

At this point it was decided to change the cell material to hot-pressed boron nitride. This material has the advantage of being non-wetting to most liquids, and of being machinable by conventional tooling. Experiments were conducted with die manufacture, and it was found that they could be made only with a minimum 2 mm wall thickness.

In the first trial, there was a rapid apparent increase in length above 600 °C, significantly below the melting point of 660 °C, followed by a rapid fall. On removal from the apparatus the die was found to have split (Figures 9 (right), 10). It is thought that this was probably due to inadequate allowance for thermal expansion mismatch between the metal sample and the die.

After proper characterisation of thermal expansion behaviour of the BN cell material, a repeat run was made with a new die and with better allowance for the thermal expansion mismatch between die and metal. This similarly showed a steep increase in length above about 610 °C, but this time was related primarily to proper melting expansion (Figure 11 (left)). The second and third cycles on the sample now adapted to the cell dimensions showed a small drops in length on melting, and then consistent behaviour as a liquid, followed by a drop in length on cooling (Figure 11 (right), 12 (left)). Some discontinuities of slope were noted for the solid part of the curve, suggesting some adhesion of the test-piece to the cell parts. However, it was clear that there had been no leakage. It is suspected that the thin oxide layer always present on aluminium helps to prevent leakage down the gap between cell wall and piston.

Table 2 - Summary of test results for pure aluminium

Parameter	This work	Estimate model, Mills et al. [2]	Reference [3]
Solid density at 25 °C, Mg m ⁻³ , estimated from mass and dimensions	2.68	2.71	
Solid density at solidus, Mg m ⁻³	2.55	2.55	
Liquid density at liquidus, Mg m ⁻³	2.405	2.42	2.39
Bulk volumetric expansion coefficient, 10 ⁻⁶ K ⁻¹	122	113	139

In the second trial very repeatable behaviour was obtained in the first cycle, the heating curve showing a sharp expansion on melting followed by linear behaviour at higher temperatures (Figure 12 (right)). The cooling curve more-or-less followed the heating curve, but with minor undercooling. The subsequent two cycles showed less expansion on melting, probably because of cylinder size adjustment from the first cycle, and increasing evidence of pistons sticking below the melting point.

Inspection of the specimens showed them to have retained a shape close to cylindrical, with only minor cavitation, typically on the ends.

The data were transferred to the Excel spreadsheet for calculating densities. A summary of the results appear in Table 2 and in Figure 13 and 14. These promising results led to the evaluation of aluminium alloys with a melting range.

4.4 Aluminium/silicon alloy 1 (LM25) in boron nitride cell

LM25 alloy which contains typically 7.5% Si and 0.4% Mg was selected as being of current interest to the casting industry. The same procedures as for pure aluminium were used, including selection of the outside diameter of the machined cylinder being approximately 2% less than the cell bore to allow for thermal expansion mismatch.

In two consecutive thermal cycles to 700 °C, the alloy appear to begin melting at about 575 °C as shown by a rapid increase in length, and was fully molten at 605 °C. Repeatable behaviour as a liquid on heating and cooling suggested no leakage. The solidification process commenced at about 605 °C and appeared complete by 575 °C. Some piston sticking was detected at lower temperatures (Figure 15).

A second sample showed very similar results (Figure 16). After extraction from the cells, both samples showed good geometry and no obvious leakage. The surface microstructure was clearly much finer than for pure aluminium, but there was minimal surface roughness due to feeding effects on cooling (Figure 17).

Output data from the cell thermal expansion computation were transferred to the spreadsheet and the various parts of the curves were separated out for analysis as described above. It became obvious that the density of the metal during melting was similar on heating and cooling, and that the trend was a curve, rather than a straight line, in keeping with the typical shapes seen in phase diagrams (Figures 18, 19). The estimated density values at the liquidus and the bulk volumetric expansion coefficients referenced to the density at the liquidus are given in Table 3, together with data from Netzsch [1] on the same alloy. The results show quite good consistency.

One feature of these data is that the apparent solidus temperature of 575 °C is significantly above the true solidus temperature, which should be about 550 °C according to differential cooling curve data [5]. One explanation is that the cell dilatometry tests show a transition from liquid to solid at a condition where the solidifying mass is essentially rigid, and can resist the pressure applied by the pistons. This would occur on cooling when the growing dendrites contact. Similarly, on heating, the corresponding point would be when this dendritic structure started to melt. The fraction of liquid phase at this point may vary according to the microstructure of the dendrites, but might typically be expected to be at about 50% liquid. For the present purposes, the point where the dendrite structure collapses is termed the "deform point".

Table 3 - Density estimates for LM25 at the melting point

Sample/ run number	Density, 25 °C, from mass and dimensions, Mg m ⁻³	Density at "deform point", Mg m ⁻³	Liquid density at liquidus, Mg m ⁻³		Volumetric liquid expansion coeff., 10 ⁻⁶ K ⁻¹	
			Heat	Cool	Heat	Cool
1, E4604, run 1	2.64 (2.67*)	2.52	2.410	2.405	120	122
1, E4604, run 2		2.52	2.413	2.412	123	124
2, E4607, run 1	2.66 (2.67*)	2.52	2.415	2.416	123	127
2, E4607, run 2		2.53	2.440	2.440	126	132
Data from Netzsch [1]	2.63	2.52	2.40		112 (estimated from plot)	

Densities estimated from compositional model (Mills et al. [2]).

4.5 Aluminium-silicon-copper alloys 2 and 3 in boron nitride cell

Further tests were made on two similar aluminium-silicon-copper alloys A and B of more complex composition. The tests were also successful, with no leakage. the apparent cell thermal expansion data and the melting curves were similar to those for LM25. The numerical results are summarised in Table 4. These alloys also show an apparent solidus, or "deform point" of about 575 °C, similar to that found in LM25. This is substantially above the true solidus temperature of ~510 °C corresponding with the eutectic reaction reported by Bäckerud et al. [5], but with a point at which there is between 30% and 40% liquid phase.

4.6 Alumina dies for higher temperature work

Overfelt and Taylor [6] have reporting disappointing results for the melting curve of IN718 (solidus 1250 °C) using a graphite cell, primarily as a result of leakage. In addition, there is a strong risk of reaction between the cell and the alloy. NPL is also aware of the work on the melting characteristics of nickel alloys by Netzsch GmbH of Germany [4] using single crystal sapphire dies, which have been used with mixed success for obtaining data on melting. The key problem with such dies is that they are extremely expensive to make, especially as they may only be usable for a single experiment. Rather than simply copying this latter approach, the possibility of making polycrystalline alumina dies for testing high-temperature alloys, such as nickel alloys, has been investigated. Within the time-frame of the present programme it has not been possible to test such dies owing to delays outside project control. The principal problem with making alumina (or indeed sapphire) dies is that, unlike Macor or boron nitride, the die material cannot be machined by normal turning and drilling to achieve the required engineering dimensions. Special diamond boring tools have to be purchased. These can then be used to ream out an as-fired, small-bore alumina tube. However, the surface finish achievable in such dies depends on the grit size of the boring tool and the stiffness of the system being used. NPL Optics Workshop has made a cell set by machining, but there are some concerns over the control of the clearance between the cell and the pistons. The machining of appropriately sized Inconel 718 alloy samples is currently in hand, but that also has suffered from delays due to machinery breakdown.

Table 4 - Density estimates for aluminium-silicon alloy during melting

Test	Start density from mass, dimensions Mg m ⁻³	Estimated density at "deform point"*, Mg m ⁻³	Estimated density at liquidus, Mg m ⁻³	Volumetric expansion coefficient of liquid, 10 ⁻⁶ K ⁻¹
Sample A1: run 1 E4613 Heat Cool	2.710 (2.708*)	2.617 2.629	2.440 2.440	118 123
Sample A1: run 2 E4613 Heat Cool		2.632 2.589	2.440 2.442	121 122
Sample A2: run 1 E4617 Heat Cool	2.718 (2.708*)	2.590 2.579	2.450 2.450	120 124
Sample A2: run 2 E4617 Heat Cool		2.614 2.609	2.463 2.463	122 123
Sample B1: run 1 E4615 Heat Cool	2.687 (2.708*)	2.583 2.575	2.402 2.408	125 125
Sample B1: run 2 E4615 Heat Cool		2.588 2.588	2.410 2.408	127 126
Sample B2: run 1 E4620 Heat Cool	2.648 (2.708*)	2.566 2.672	2.432 2.430	119 127
Sample B2: run 2 E4620 Heat Cool		2.554 2.568	2.391 2.391	123 125

Densities estimated from mechanical model (Mills et al.)

Very recently, NPL was made aware of technology at Friedrichsfeld GmbH of Germany for manufacturing monolithic alumina ceramic metering pumps for the food and drugs industry, comprising cylinder and piston arrangements. The facility has the capability of manufacturing precise pump sets with polished pump body bores and piston surfaces. NPL has organised the purchase of several such pump systems for re-machining into dilatometric cell sets. However, the delivery of such pumps is outside the duration of the project. It is hoped that this manufacturing technology can be used to explore the possibility of high-temperature dilatometry in the future.

5 DISCUSSION

5.1 Cell behaviour

It is clear from the experimental work undertaken on low-temperature metals and alloys that reliable results can be obtained only if the cell/piston arrangement does not leak, such that the effective mass of material between the pistons remains constant and therefore known. With conventional machined surfaces obtained on machinable ceramics by turning, drilling and reaming, there are limitations to the smoothness of finish, and hence to the ability of the pistons to slide with a minimum of friction or risk of jamming. The possibility of using metering pump technology for preparing cell sets with polished surfaces is an important aspect to continue to investigate.

Both Sn and Sn/In test-pieces leaked from the machinable ceramic cells to varying degrees, despite the closeness of the fit of the pistons to the cell. In most cases beads of metal typically 0.5 mm to 2 mm diameter were found in the dilatometer, having exuded down the gap. On removing the test-piece from the cell, thin foils of metal were found in the piston/cell gap, suggesting that the surface tension of these metals is very low, and the push-rod force required to move the piston is too high to prevent leakage. No sensible data could be obtained from these runs. Similar problems have been reported for nickel alloys [6].

In contrast, aluminium and aluminium alloys have been successfully tested using a boron nitride die. The advantage of aluminium is probably the existence of a thin oxide film under all conditions and, together with the non-wetting character of the boron nitride cell material, this must help prevent leakage. Boron nitride cells could be used several times, but even so, some interaction did occur resulting in adhesion between the solidified sample and the cell wall, probably through the oxide interlayer.

5.2 Behaviour of metal alloys in the cell

It is clear from the successful runs undertaken so far that for the accurate following of melting behaviour there are a number of conditions that must be fulfilled:

- 1 Minimal reaction between the metal and the cell leading to inability of the pistons to slide smoothly and thus follow the melting behaviour.
2. Sufficient, but not excessive, pressure applied to the pistons to ensure that the cell diameter is filled.
3. No significant leakage or movement of metal along the piston/cell gap.

Once these are fulfilled, the cell should follow the melting and subsequent solidification behaviours at the desired heating/cooling rates. However, it is becoming clear that the apparent start of melting in alloys with a melting range is at a temperature significantly above that predicted by, for example, differential scanning calorimetry and cooling curves. This must be due to the continued rigidity of the higher-melting dendritic structure that first crystallises out on cooling. The true melting curve can only be identified above the temperature at which this dendritic structure gives way and permits the full cell volume to be filled, and hence the piston displacement accurately to follow the process. The volume fraction of liquid required to achieve this condition is not known, but might reasonably be expected to be about 50%. This figure may be influenced by the nature of the dendritic structure developed, which may

be a function of composition. Although in some respects this is disappointing, it does have some realism in casting conditions, except in cases where high pressure is applied to ensure conformance with the die geometry. This work has named this temperature "deform point", and this is probably fairly sharply defined for a given alloy composition.

Unlike industrial casting processes, it is not possible with the cell system to maintain significant pressure on the melting or solidifying alloy because of the risk of leakage, consequently, the data appear to have validity only for liquid and mushy zone behaviour down to the "deform point". This work has shown that this behaviour can be followed quite accurately and repeatably, at least for aluminium alloys. Below this temperature, the remaining liquid continues to solidify and to shrink, and the liquid is thus drawn into the bulk of the test-piece. This initially leaves the surface with a dendritic pattern standing proud, but latter can in principle lead to cavitation. The use of small test-pieces cooled slowly is thought to minimise this problem, which can be overcome only by applying pressure to the casting in order to "feed" more liquid into the space defined by the dendritic structure. Assuming that the test-piece prepared for the experiments is essentially void free, the relative reliability of data below the deform point on cooling and during a second or subsequent thermal cycle must be poor. This is discussed at greater length below.

5.3 Accuracy analysis

One of the important factors in assessing the value of the technique is the likely accuracy levels achievable. There are a number of contributory factors:

1. *Accuracy of measurement of cell thermal expansion behaviour.* Using a boron nitride cell, the expansion coefficient is very low, and makes a negligible correction to the overall data. Alumina cells have a significant thermal expansion contribution, which might typically be of the order $\pm 1\%$ in terms of the final density calculations.
2. *Accuracy of measurement of starting density of the alloy.* The present work used mass and dimensions for calculating densities, which were within about 1% of the recognised densities obtained by immersion methods on larger test-pieces. This item of data is used as a reference for defining the volume of the metal in the cell (assuming no leakage, and hence constant mass) and directly affects the liquid densities through the use of equation 23.
3. *Accuracy of the room temperature dimensions of the cell.* The bore diameter is particularly difficult to measure accurately. Using a travelling microscope, an accuracy of about ± 0.02 mm is achievable based on sighting on the ends, but the cell may well not have uniform bore. For a 6 mm bore cell, this is an error of about 0.3%, or 0.6% in cross-sectional area.
4. *Any tendency of the pistons to jam* as a result of development of interaction with the metal, such as the development of oxides or other interlayers. This has to be taken on a case by case basis, and is likely to be revealed by differences between heating and cooling curve shapes, or discontinuities in behaviour. Such runs should be ignored, the cell refurbished, and the experiment repeated.
5. *Temperature measurement.* The thermocouple measuring cell temperature can be placed only on the external wall of the cell. With a poor thermal conductivity cell, the temperature difference between this thermocouple and the cell contents will depend

on the heating/cooling rate, but is typically expected to lead the cell internal temperature by about 1 °C, except where melting or solidification are sufficiently rapid that a significant endotherm or exotherm are respectively produced. The slower the thermal cycle, the more accurately temperatures are likely to be measured.

One factor that was initially thought to be critical was the need to ensure that the cell was essentially filled at the onset of melting, so there was no uncontrolled apparent reduction in length counteracting the increase in length due to the density change on melting. In practice, the analysis has shown that this is unimportant, and the reference point is in fact the density at room temperature.

Overall, the total error on calculating density above the "deform point" would seem to be about $\pm 2\%$. The error in liquid bulk expansion coefficient is also thought to be of similar order.

6. CONCLUSIONS

This study has evaluated the use of pistons cells for determining melting/solidification behaviour of metal alloys, and has developed a rigorous analysis of the behaviour of a melting metal in a cell system. It has shown that the principle works reasonably well provided that the cell is correctly designed and finished in such a way as to avoid leakage and at the same time minimise friction effects between the pistons and the cell wall.

The method appears to have worked successfully for a range of aluminium alloys, and has demonstrated that melting and solidification behaviour above a so-called "deform point" can be determined. It is conjectured that this "deform point" is the temperature at which melting has progressed sufficiently that the dendritic network of the higher-melting phase collapses, or on cooling, at which this network impinges on itself and become rigid. Below this temperature, continued solidification could lead to liquid being drawn into the test-piece from the surface, and where this is restricted, surface collapse or internal cavitation may occur.

The use of the method for pure aluminium with no melting range also appears possible, although the risks of cavitation are more significant.

The successful application of the method to aluminium and aluminium alloys may be reliant on the development of a thin oxide skin and the use of a non-wetting boron nitride die. Tests on tin and a tin/indium alloy using a machinable glass-ceramic cell were not successful due to cell leakage. However, sufficient indications were obtained to give some confidence that with improved quality of cell bore and piston surface finish, permitting a closer dimensional match and a narrower gap between pistons and cell wall, reliable behaviour could be achieved.

No tests with high-temperature alloys were feasible during the project schedule owing to delays in acquiring both cells and test-pieces. However, a possible source of high-quality cells has been identified, and experiments will be conducted when these are finally delivered.

Acknowledgements

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References

- [1] Henderson, J.B.; Blumm, J.; Hageman, L., "Measurement of the thermophysical properties of an aluminium-silicon casting alloy in the solid and molten regions", Netzsch-Gerätebau GmbH report TPS No. 1-4E, June 1996.
- [2] Mills, K.C., Quedstedt, P.N., NPL internal information.
- [3] Kawai, Y.; Shirashi, Y., *Handbook of physico-chemical properties at high temperatures*, Iron and Steel Institute of Japan, 1989.
- [4] Henderson, J.B., Netzsch Gerätebau GmbH, personal communication, October 1997.
- [5] Bäckerud, L.; Chai, G.; Tamminen, J., *Solidification characteristics of aluminium alloys*, AFS/Skanaluminium, 1990, ISBN 0-87433-119-6.
- [6] Overfelt, R.A.; Taylor, R.E., "Thermophysical property measurements for casting process simulation", *Thermal Conductivity* **23**, Technomic Publishing Inc, Switzerland, 1996, pp 538-549.

Sample E4582 Macor mould material, run 3

Date- 110497

Max Temp 750 C

Heating Rate 2 K/min

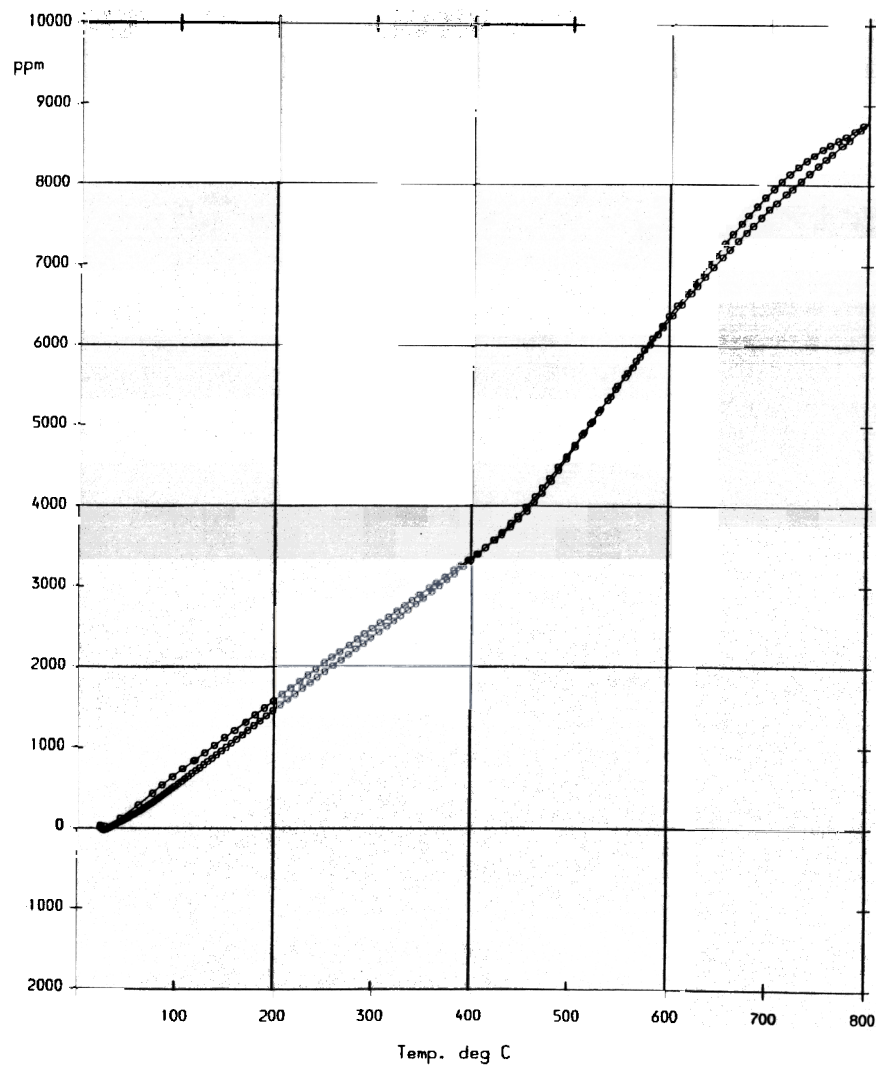


Figure 1 Thermal expansion plot of Macor mould material alone using the basic thermal expansion programme.

Sample E4595 BN cell fragment alone, run 4

Date- 31197

Max Temp 650 C

Heating Rate 2 K/min

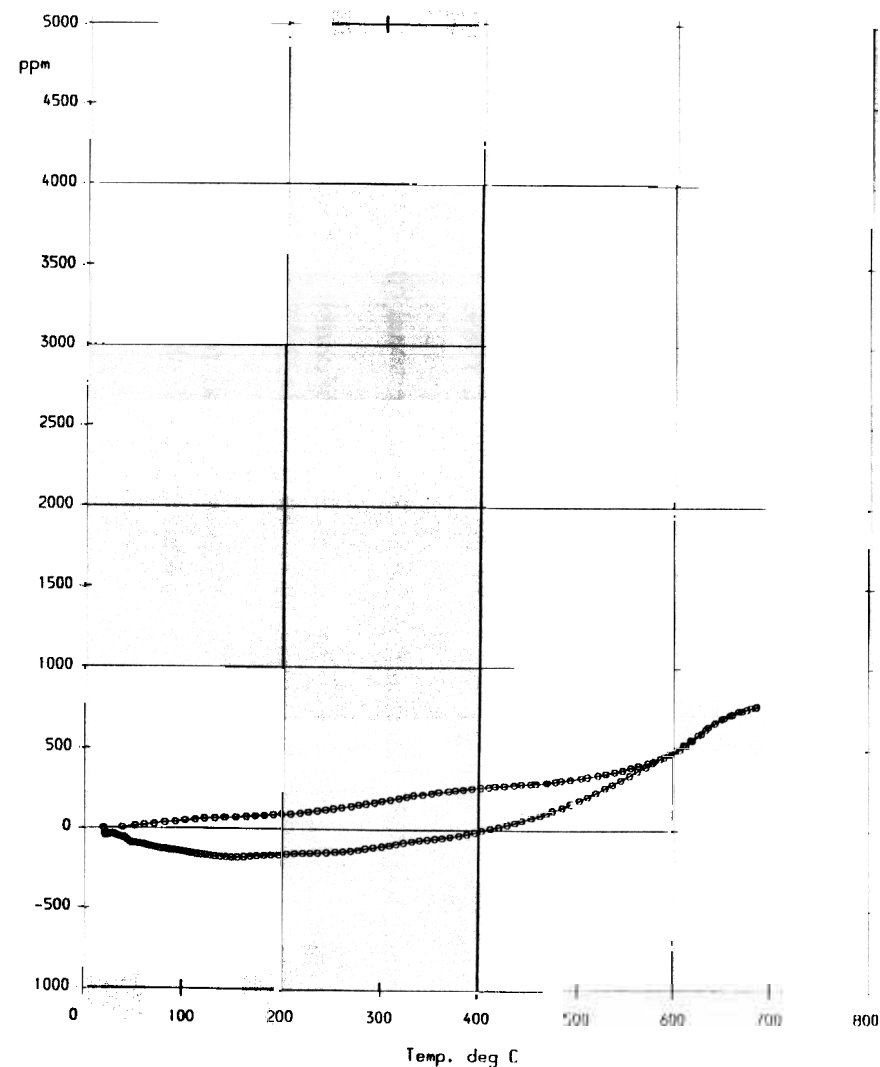


Figure 2 Thermal expansion plot of boron nitride mould material alone using the basic thermal expansion programme.

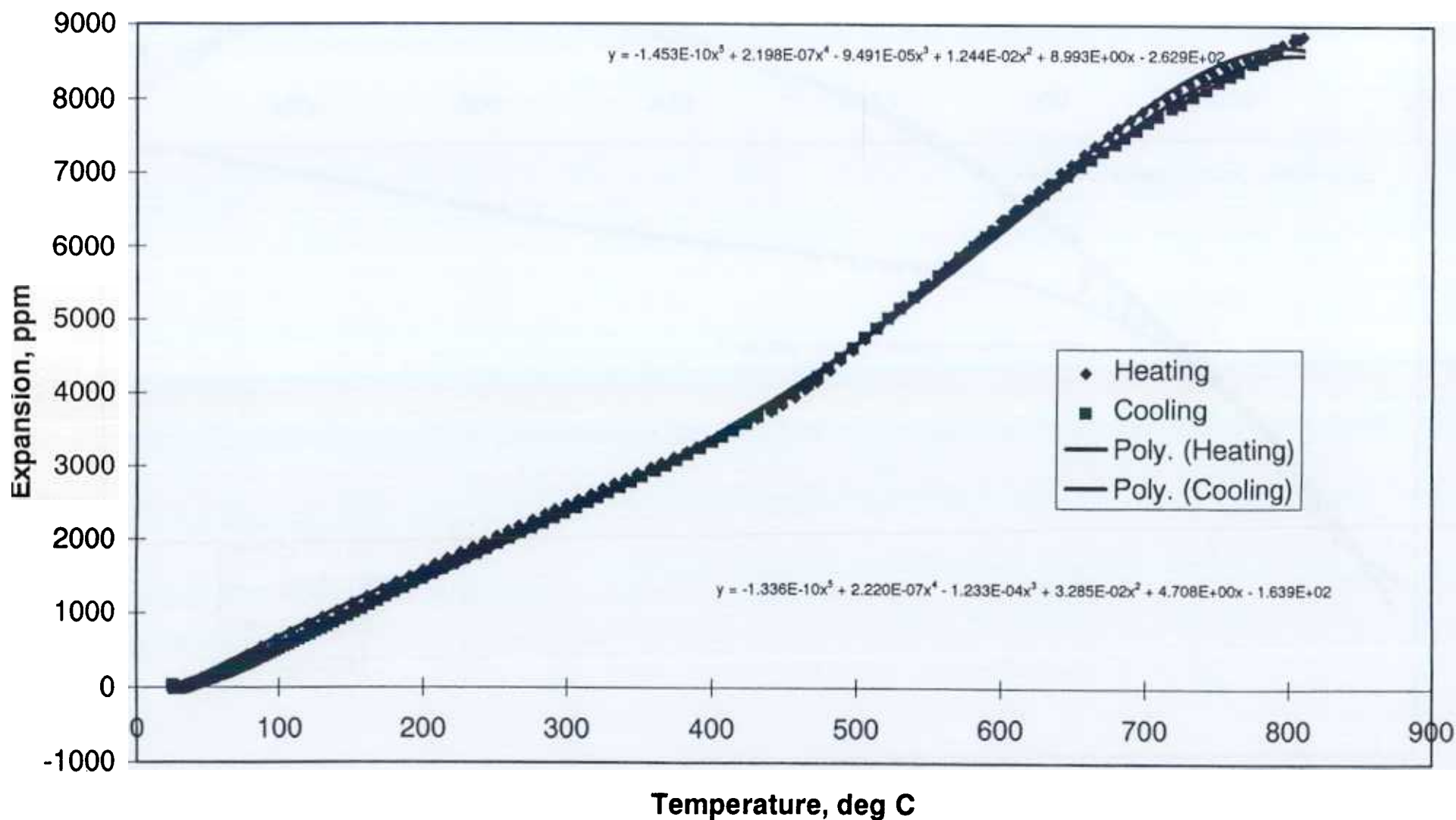
Macor run 3

Figure 3 Curve-fitting the Macor thermal expansion data separately for heating and cooling. At least a fifth order polynomial as required to achieve a good fit up to 700°C.

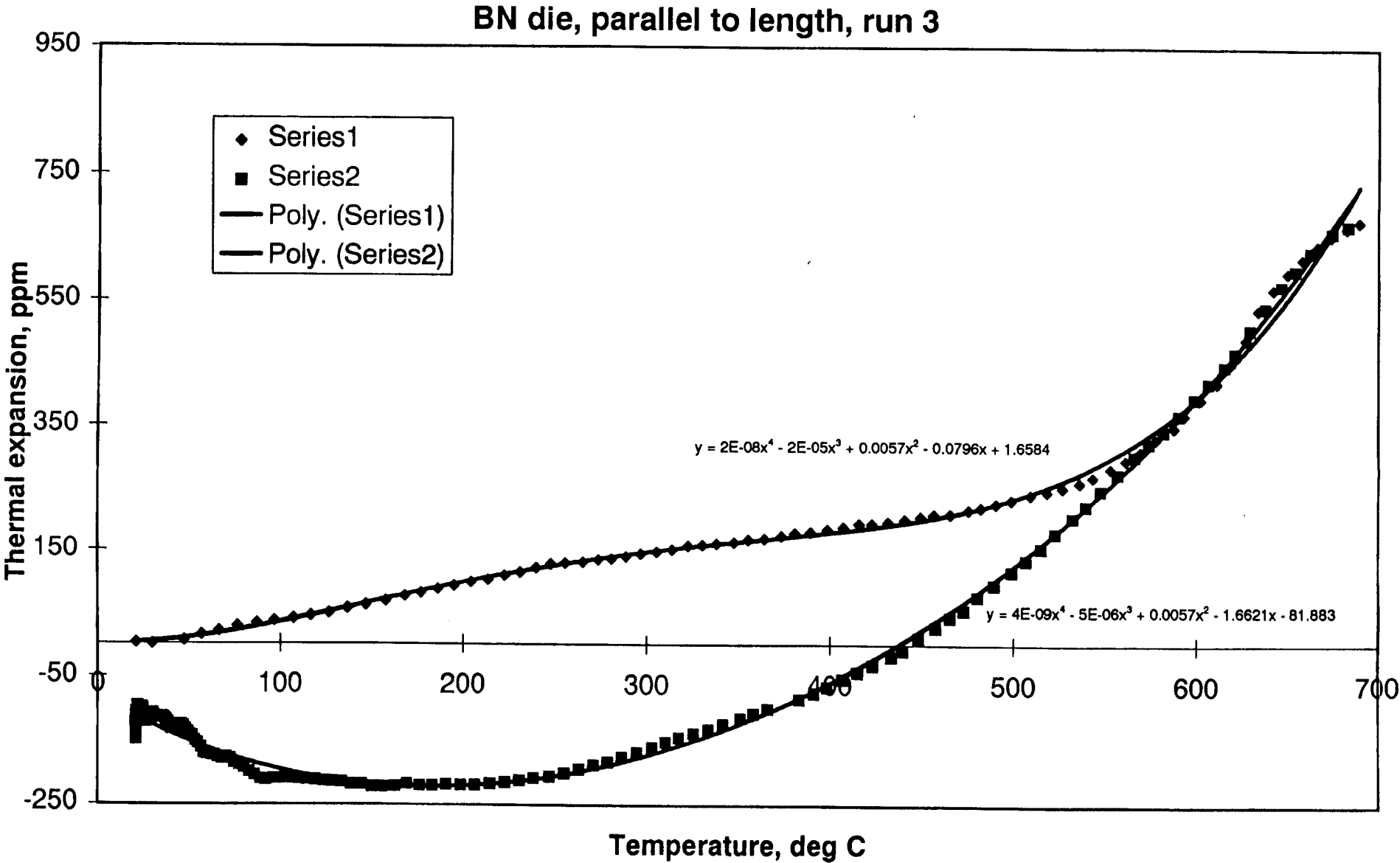


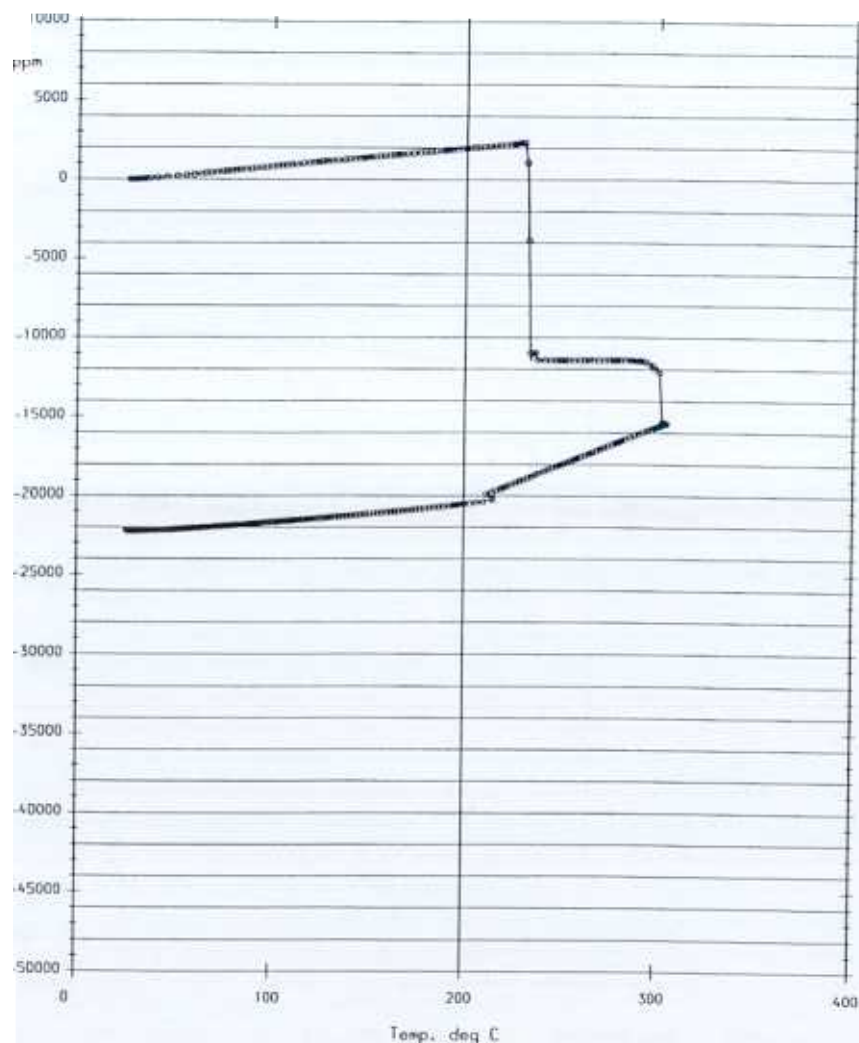
Figure 4 Curve-fitting the boron nitride thermal expansion data separately for heating and cooling. At least a fourth order polynomial as required to achieve a good fit up to 700°C.

Sample E4584 Tin in Macor cell, assumed length, run 2

Date- 140897

Max Temp 250 C

Heating Rate 1 K/min



Sample E4585 Tin in Macor cell, graphite on pistons, run 3

Date- 150897

Max Temp 250 C

Heating Rate 1 K/min

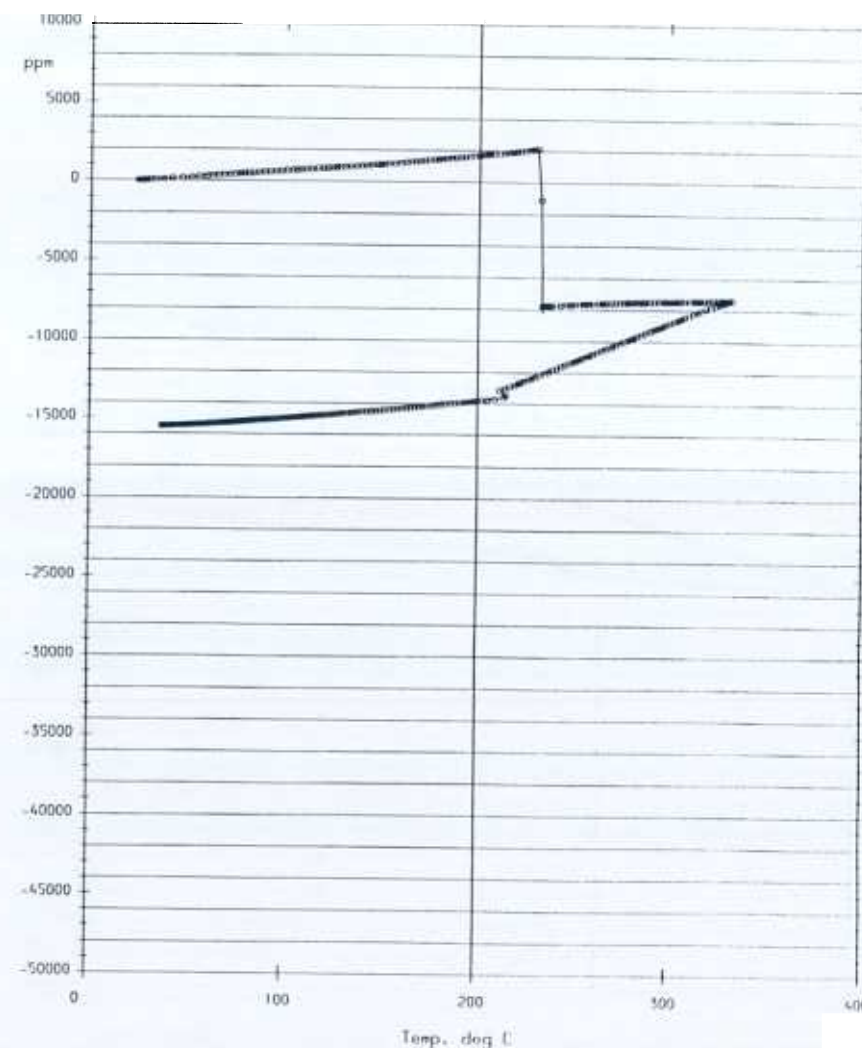


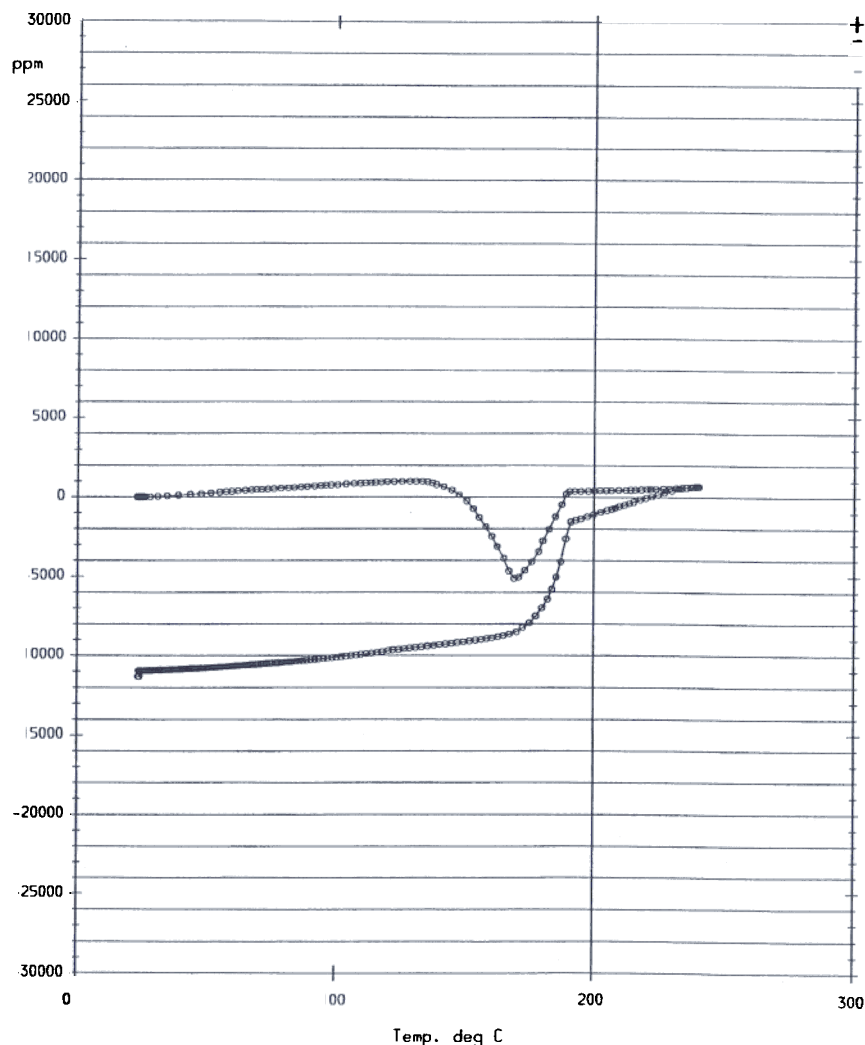
Figure 5 Cell thermal expansion behaviour for a tin sample in a Macor cell. The sample collapsed off-scale at 220 °C in the first cycle (not shown). The second cycle is shown above, left, indicating a smaller contraction on melting and no liquid expansion on heating, but a significant liquid contraction on cooling, with solidification at about 210 °C. On the right is a third cycle, this time using graphite spray to attempt to reduce leakage, but showing similar behaviour to the second cycle.

Sample E4590 In/Sb in macor cell, trial 1

Date- 151097

Max Temp 200 C

Heating Rate 1 K/min



Sample E4590 In/Sb in macor cell, trial 1, repeat

Date- 161097

Max Temp 200 C

Heating Rate 1 K/min

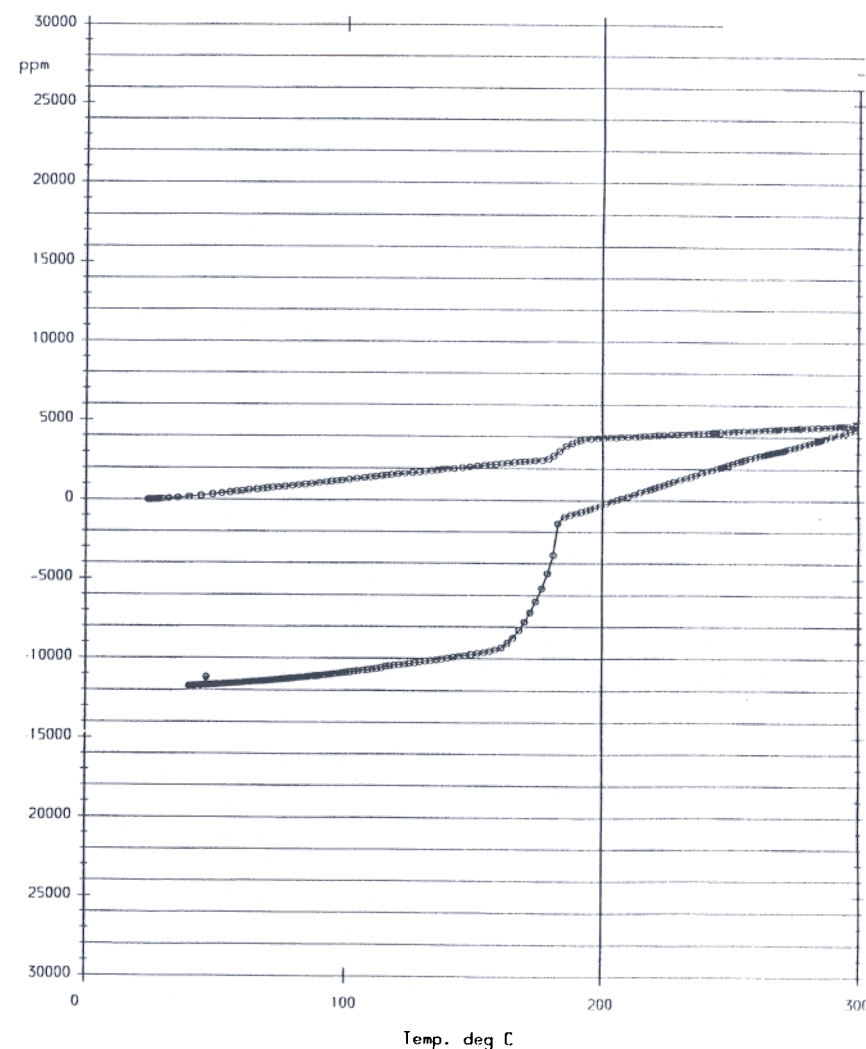


Figure 6 Cell thermal expansion behaviour for an In/Sb sample showing (left) softening and cell filling on heating, followed by melting expansion complete at 190 °C and liquid expansion at higher temperatures. On cooling the liquid contraction curve is steeper than on heating indicating some leakage. Solidification commences at about 190 °C and the sample rigidises at about 170 °C. On the right, is the second cycle without the melting drop and expansion, but the cooling curve is similar.

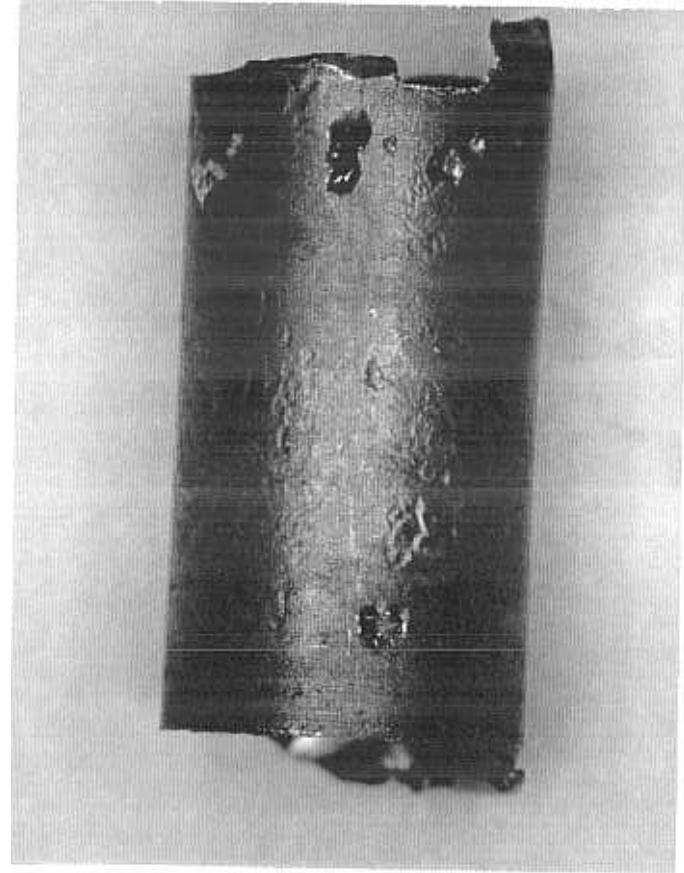


Figure 7 Photographs of (left) tin test-piece with Macor cell and pistons after the first thermal cycle showing leakage down the pistons/cell gap and some collapse on cooling and (right) the same test-piece showing evidence of liquid being drawn in on cooling leaving surface voids.

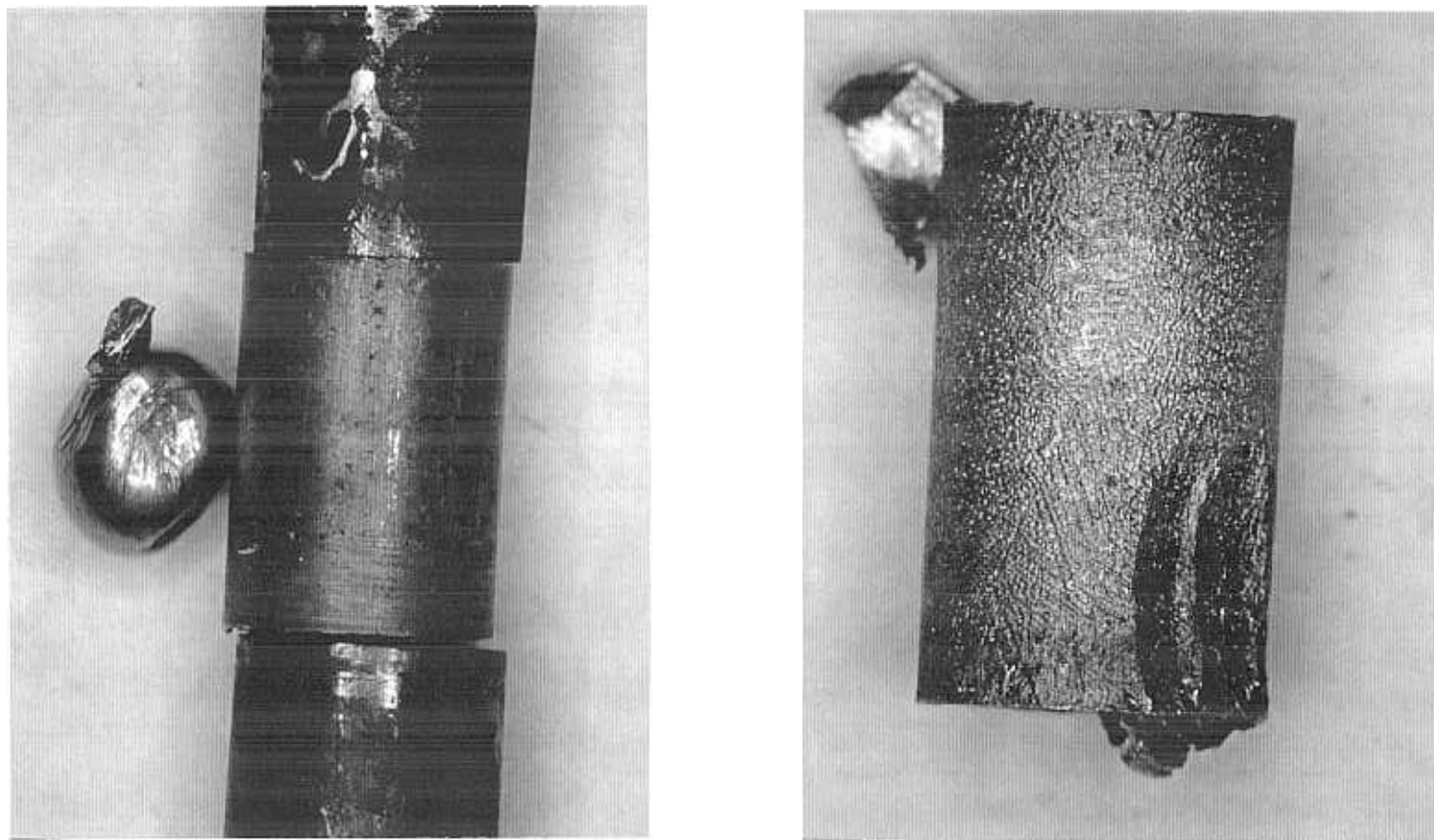


Figure 8 Photographs of (left) a second trial using tin with the exuded metal due to leakage despite using graphite on the pistons; (right) an In/Sb sample after two thermal cycles showing dendritic surface structure and thin attached foils due to leakage.

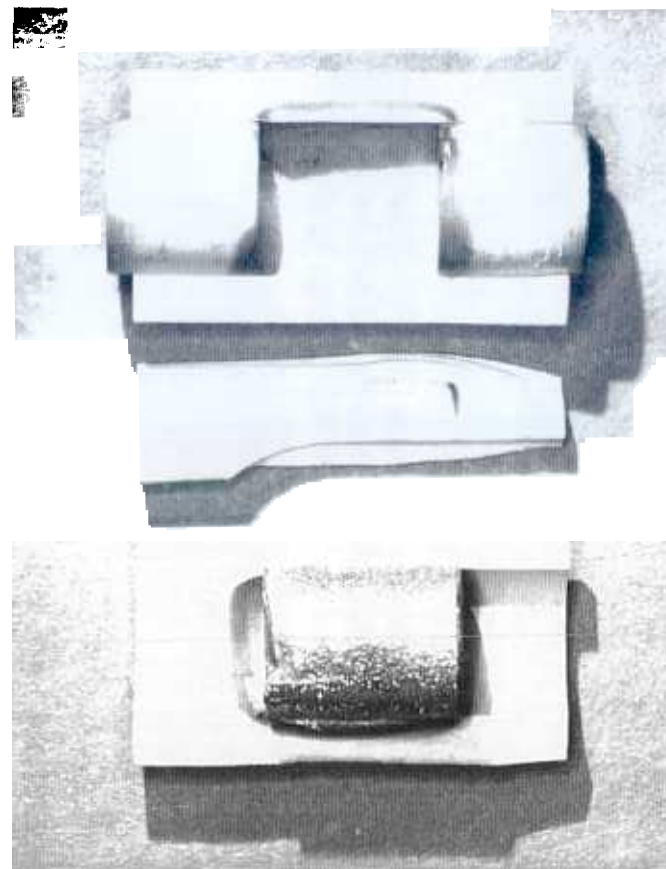
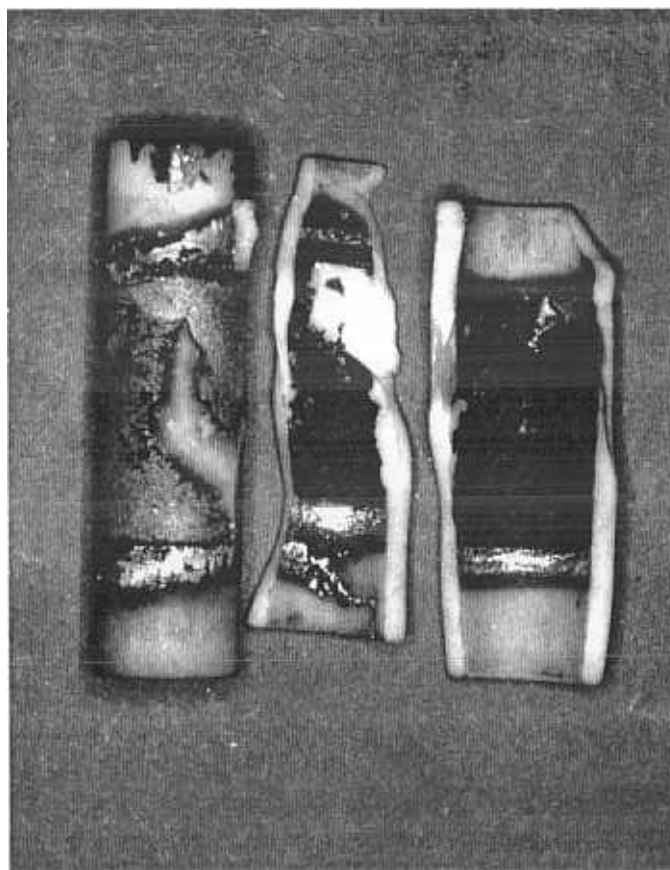


Figure 9 (Left) reaction between aluminium alloy and Macor cell following a first trial. The sample could be extracted only by breaking the cell; (right) split boron nitride cell following use on an aluminium sample due to inadequate allowance metal thermal expansion.

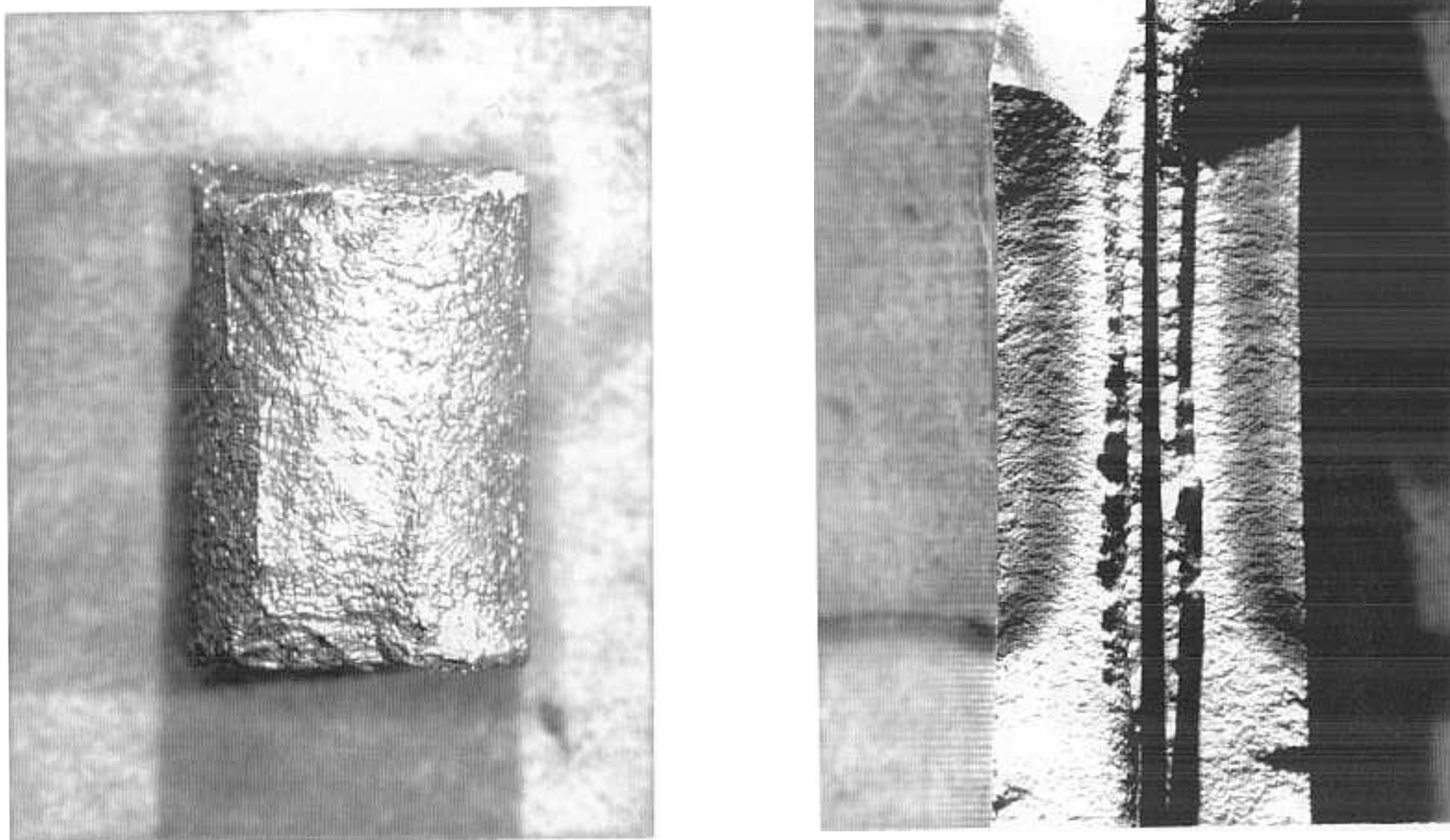


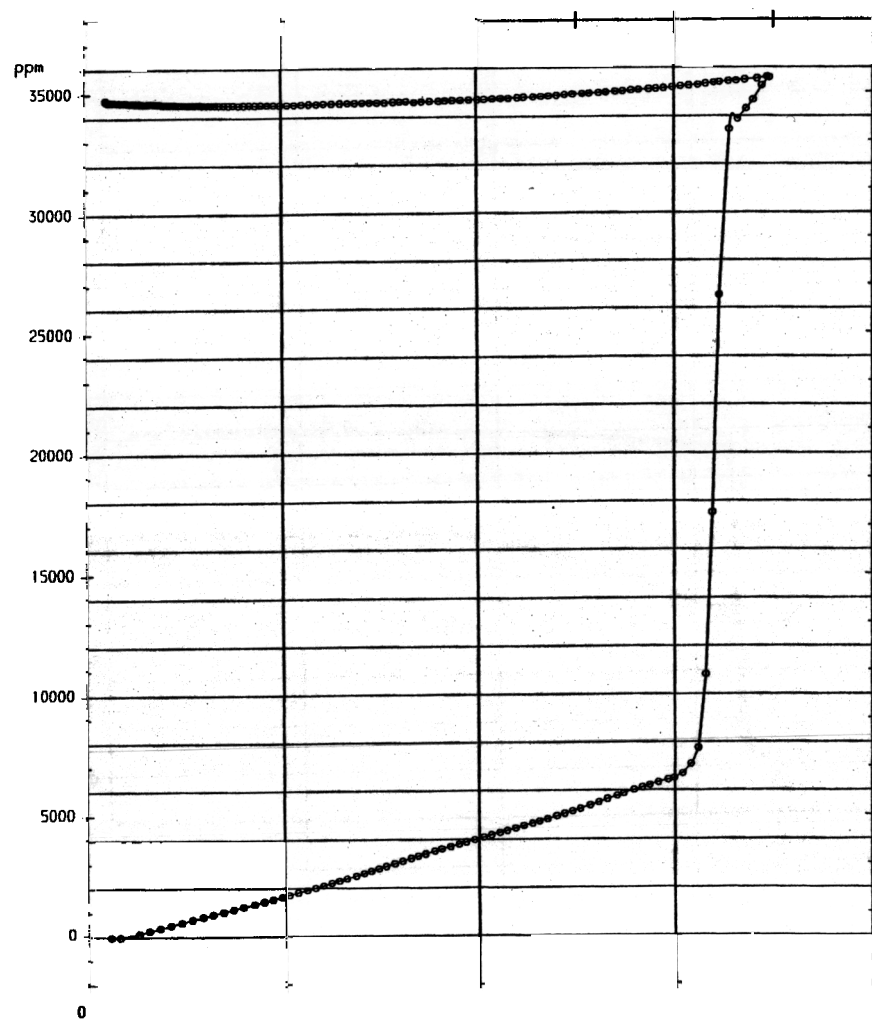
Figure 10 (Left) aluminium sample from split boron nitride cell (Figure 9) showing granular surface and general shape retention despite cell failure; (right) fractured cross-section of the cell wall showing discoloured zone (possibly reduction) despite non-wetting behaviour.

Sample E4597 Aluminium metal in BN cell run 1 in Ar

Date- 51197

Max Temp 650 C

Heating Rate 2 K/min



Sample E4597 Aluminium metal in BN cell run 2 in Ar

Date- 61197

Max Temp 650 C

Heating Rate 2 K/min

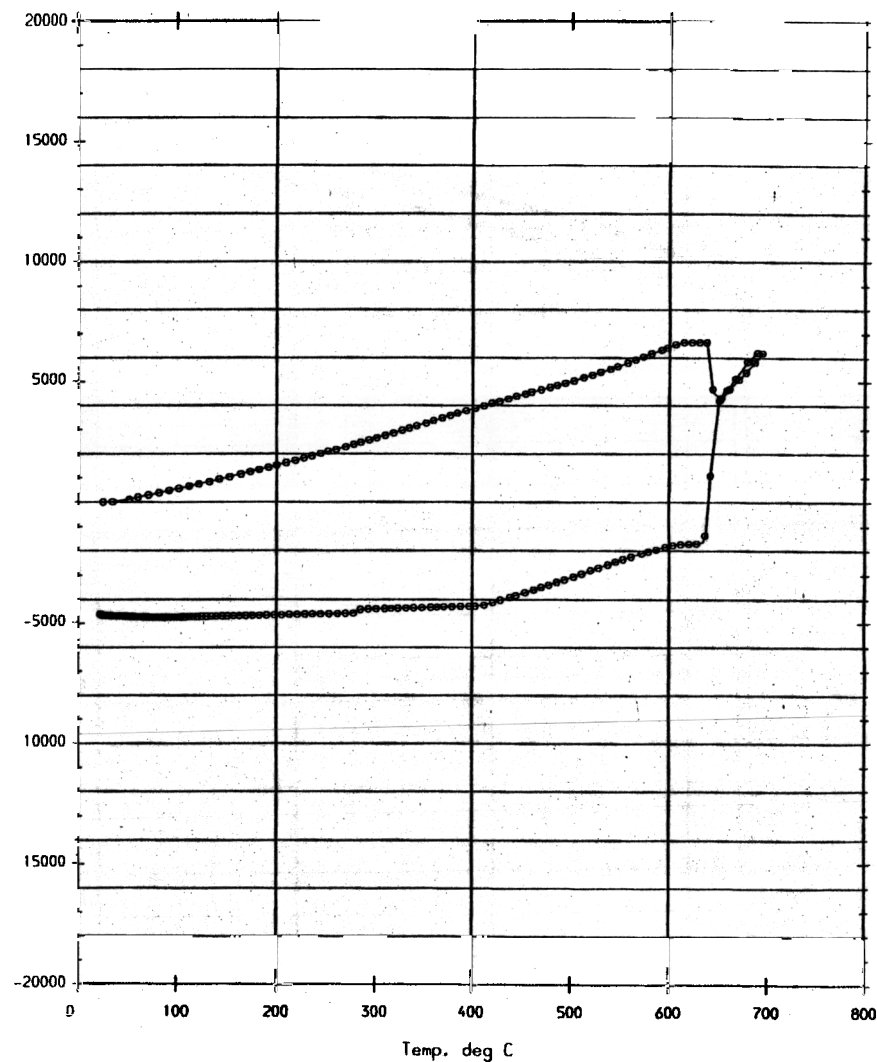


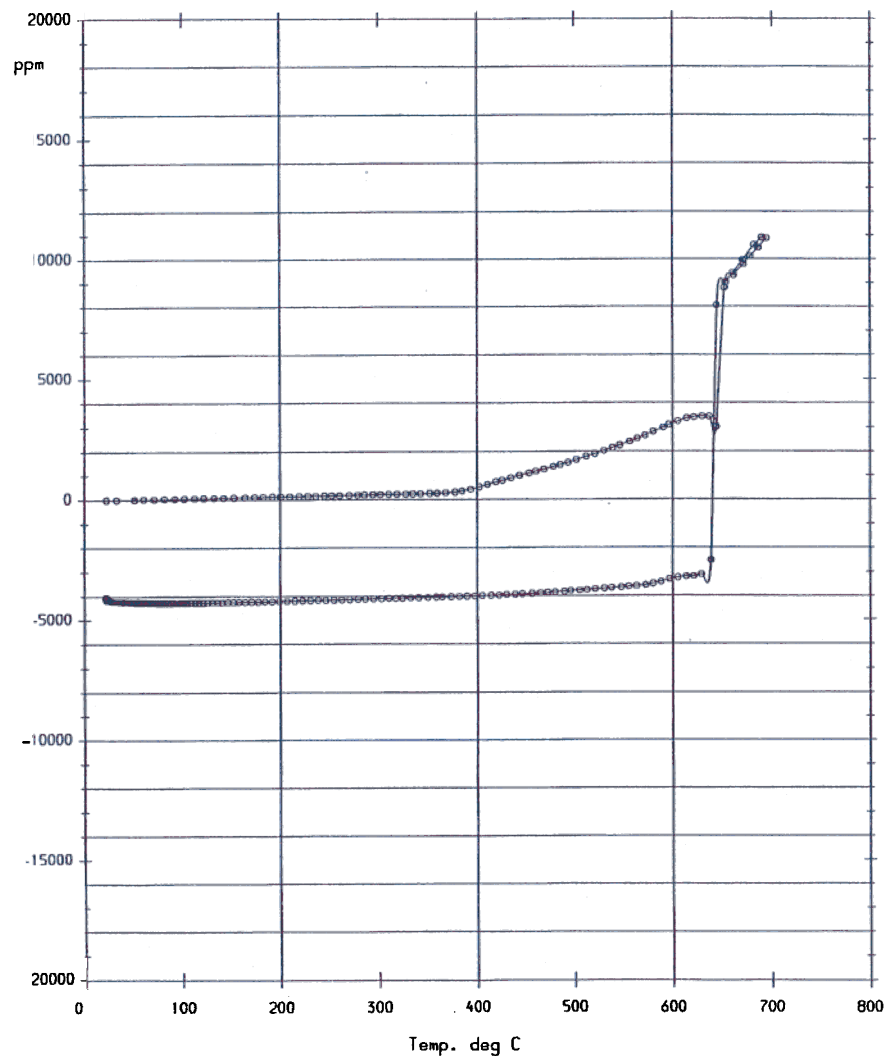
Figure 11 Cell thermal expansion for aluminium in a boron nitride cell (left) first cycle showing a sharp increase in apparent length on melting which has led to dilatometer displacement transducer being off scale; (right) second cycle showing a small drop in length on melting with consistent liquid expansion and contraction behaviour. The non-linearities on cooling are probably due to adhesion effects in the cell.

Sample E4597 Aluminium metal in BN cell run 3 in Ar

Date- 71197

Max Temp 650 C

Heating Rate 2 K/min



Sample E4603 Pure aluminium in BN die, run

Date- 41297

Max Temp 700 C

Heating Rate 2 K/min

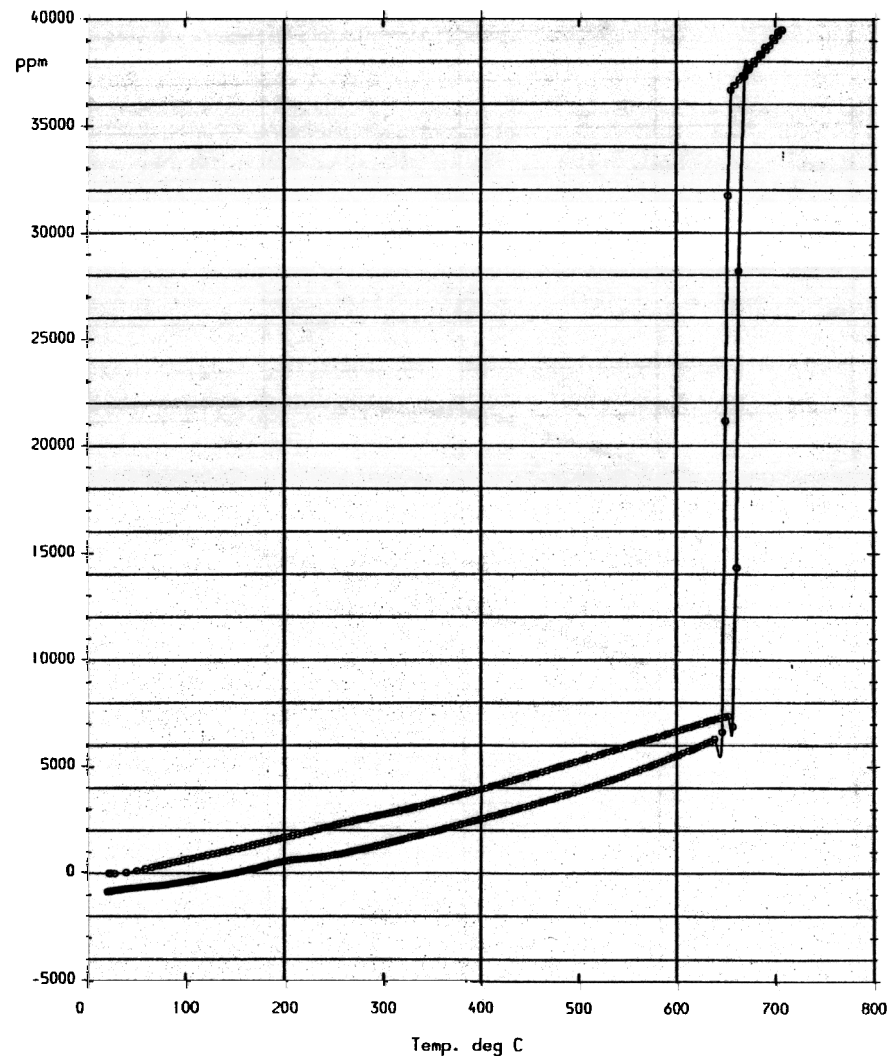


Figure 12 Cell thermal expansion for aluminium in a boron nitride cell showing (left) third cycle following those in Figure 12, and (right) a single cycle on a new test-piece.

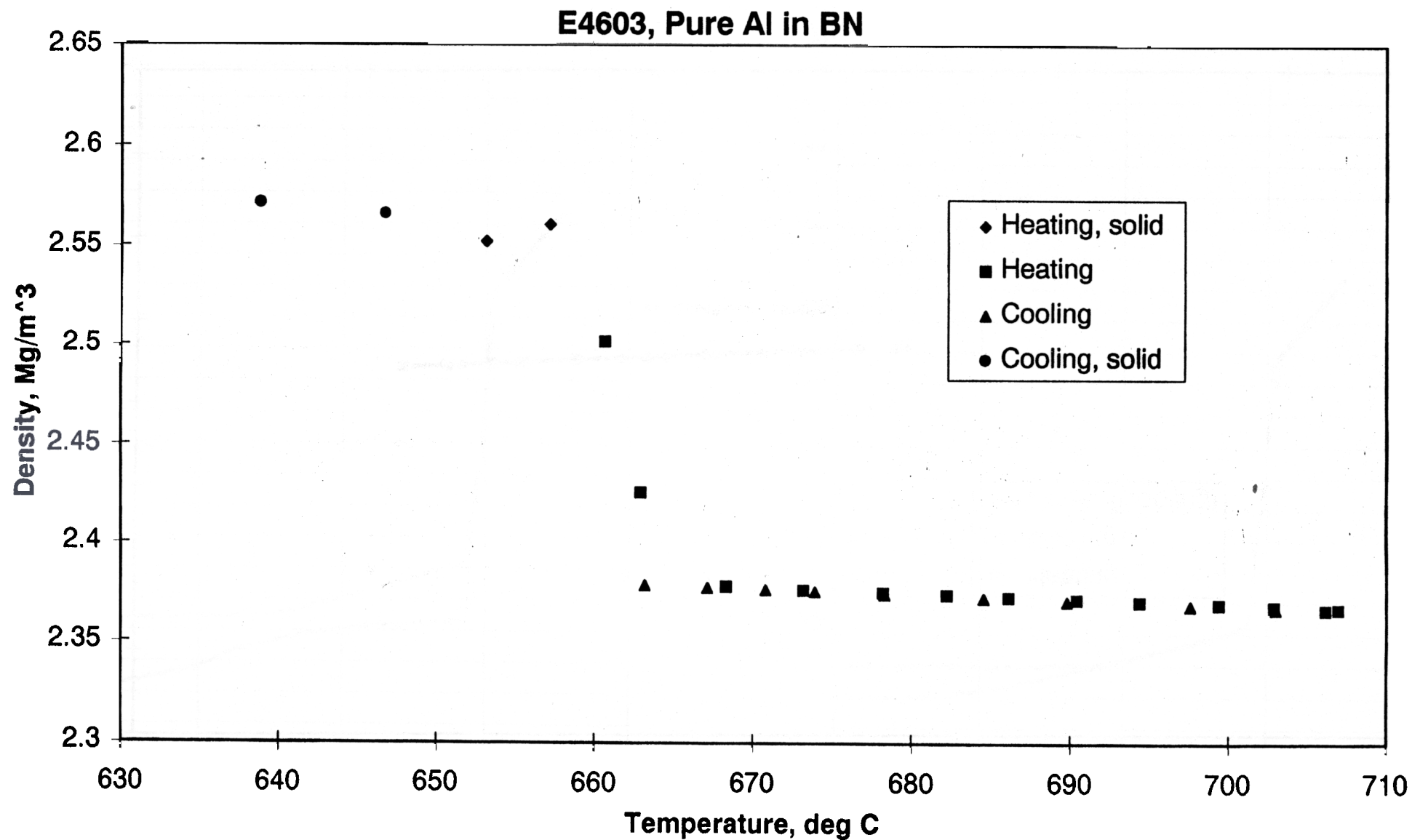


Figure 13 Calculated densities during melting and solidification for the second run on an aluminium sample in a boron nitride cell.

E4603, pure Al in BN die, run 1

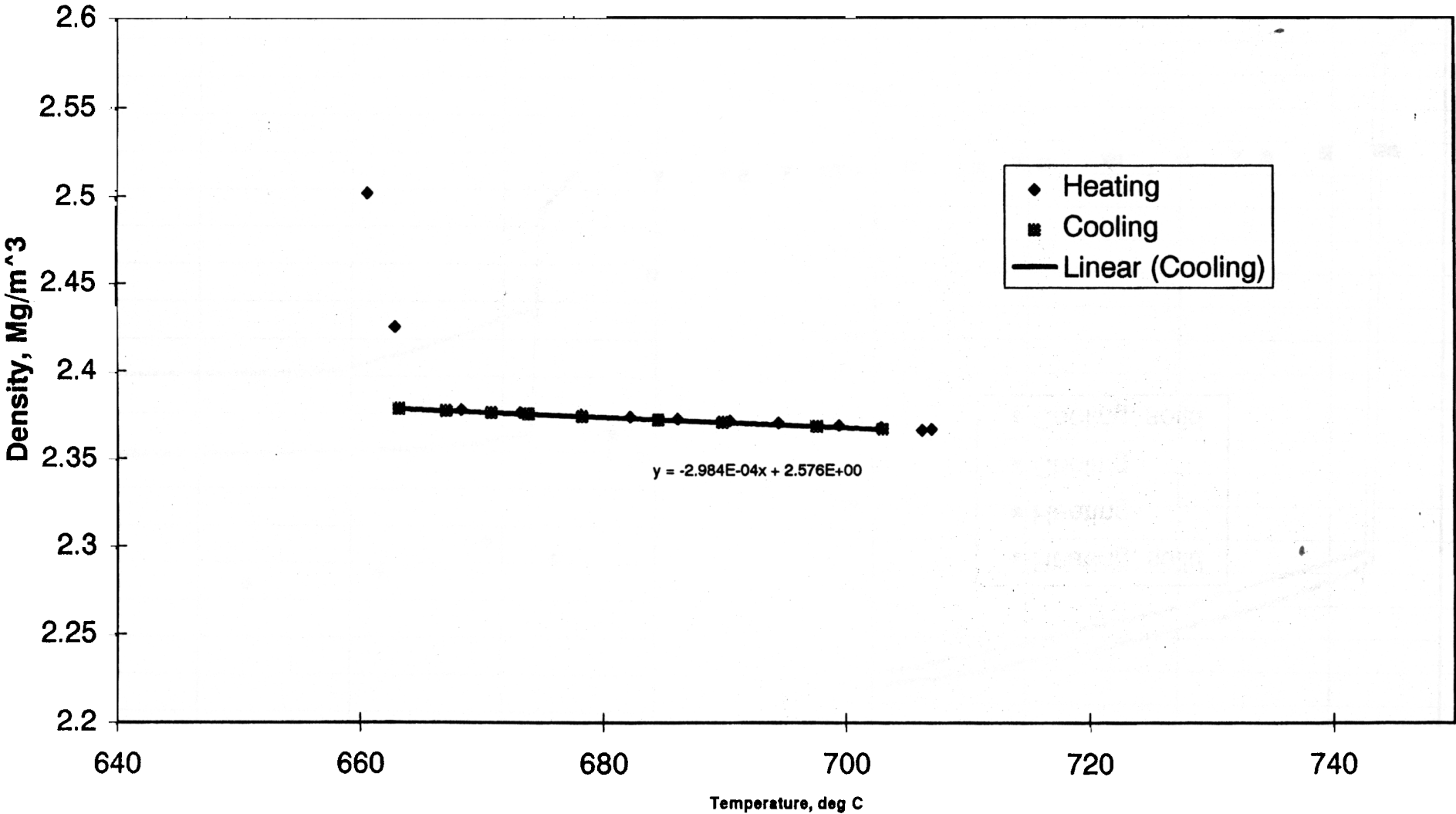


Figure 14 Estimate density as a function of temperature for molten aluminium in a boron nitride cell with separate curve fitting for heating and cooling.

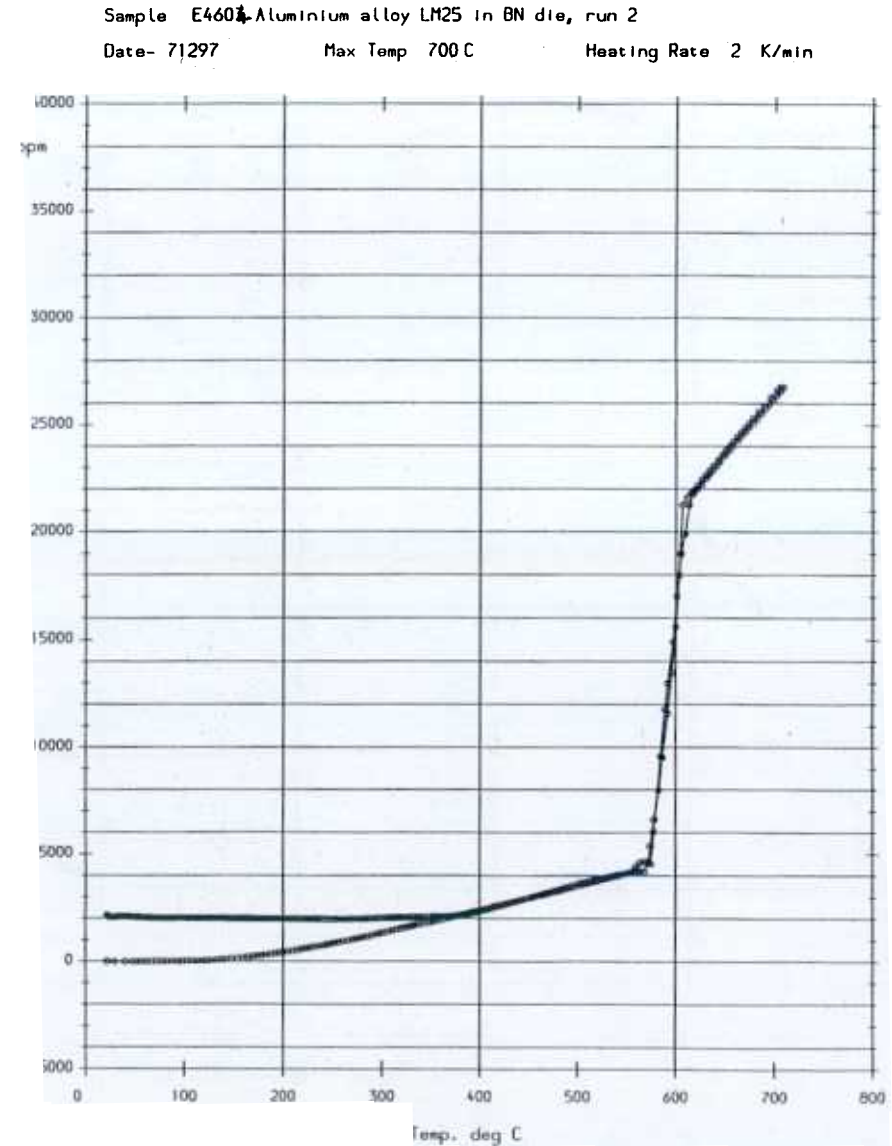
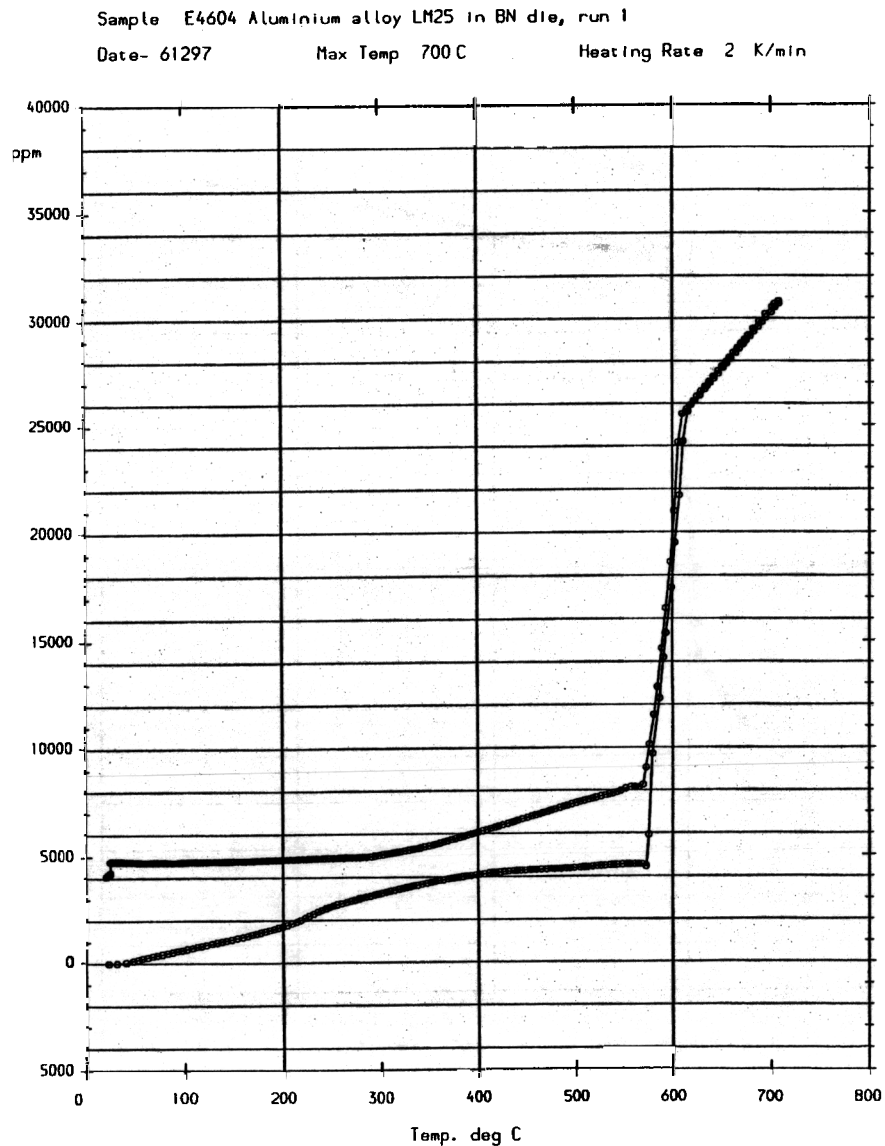


Figure 15 Cell thermal expansion behaviour in two thermal cycles for LM25 alloy sample, showing a distinct melting range and repeatable behaviour in both the liquid and mushy zones. Melting appears to commence and solidification finish at about 575 °C.

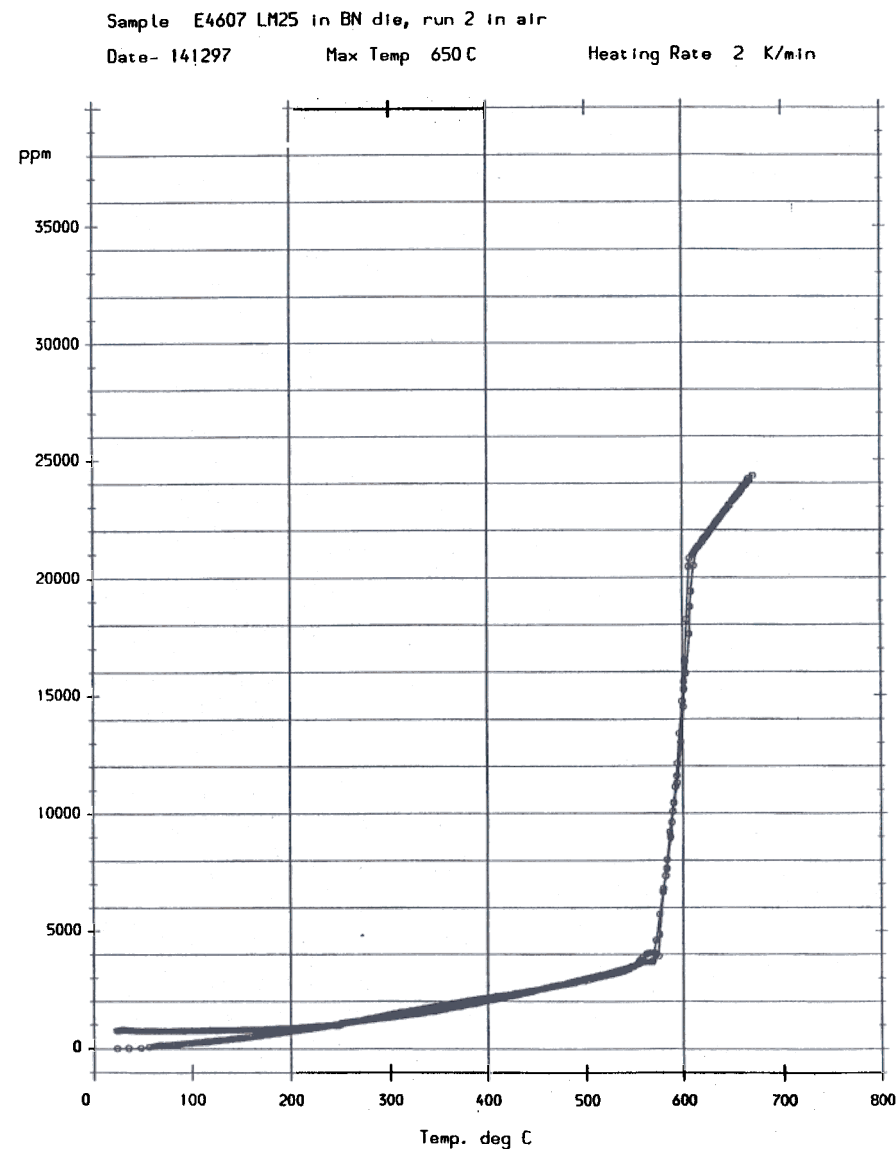
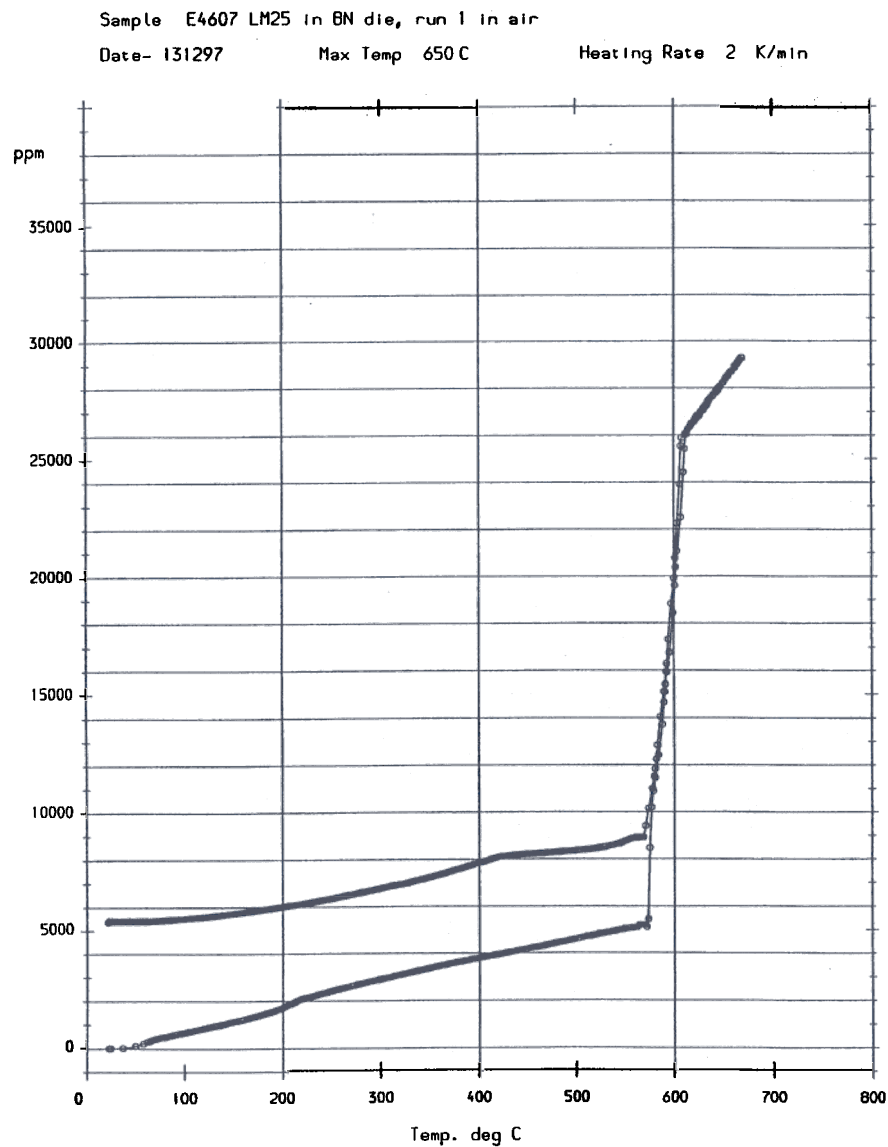


Figure 16 Cell thermal expansion results for a second two-cycle experiment with LM25 alloy, showing similar results to Figure 15.

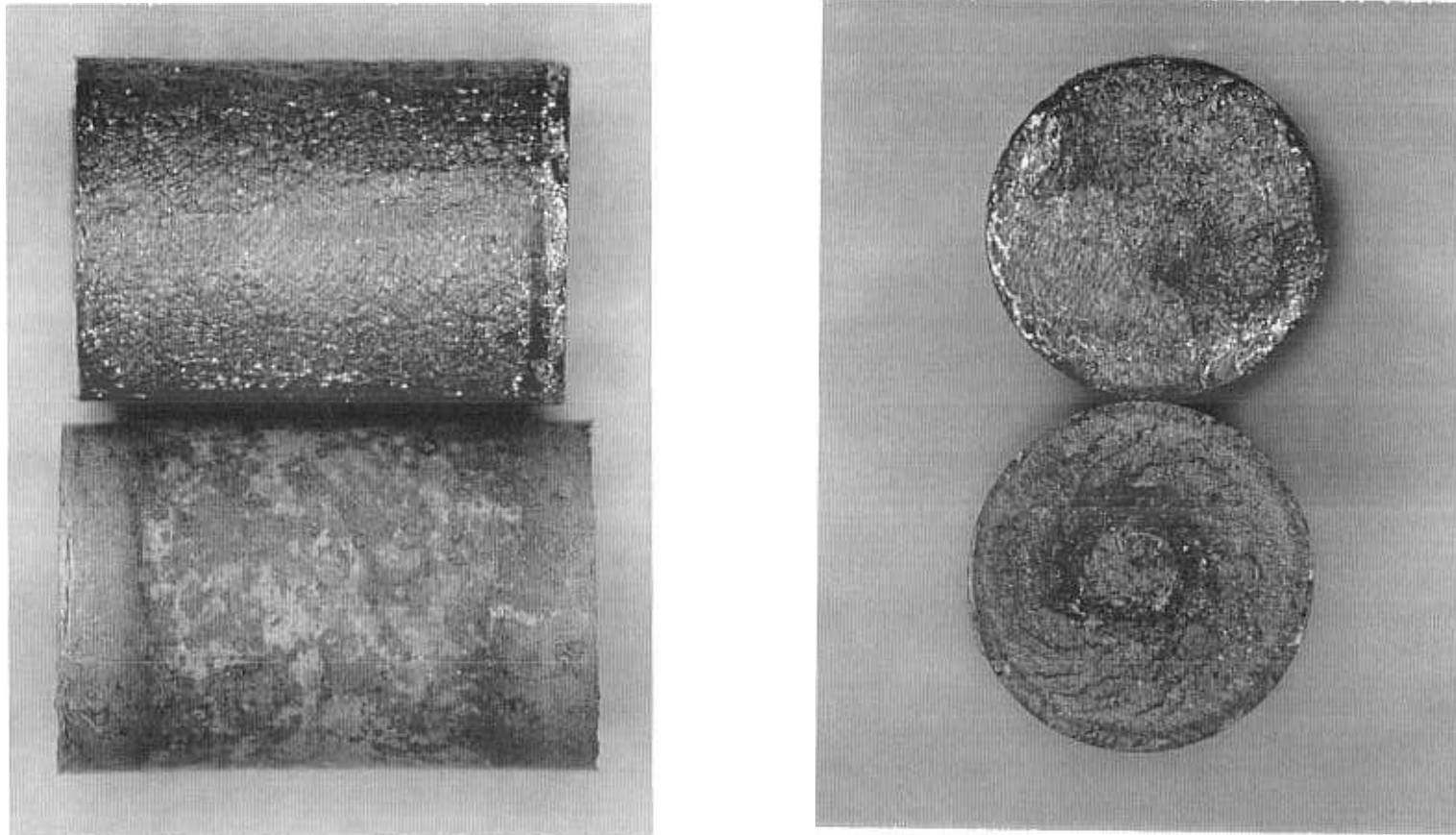


Figure 17 Photographs of the pure aluminium (top) and LM25 alloy (bottom) test-pieces after two thermal cycles in a boron nitride cell. The pure aluminium has a granular surface structure, while that of the LM25 is much smoother. There is evidence of some surface relief on the end faces due to continued liquid contraction after the rigid shape is attained on cooling.

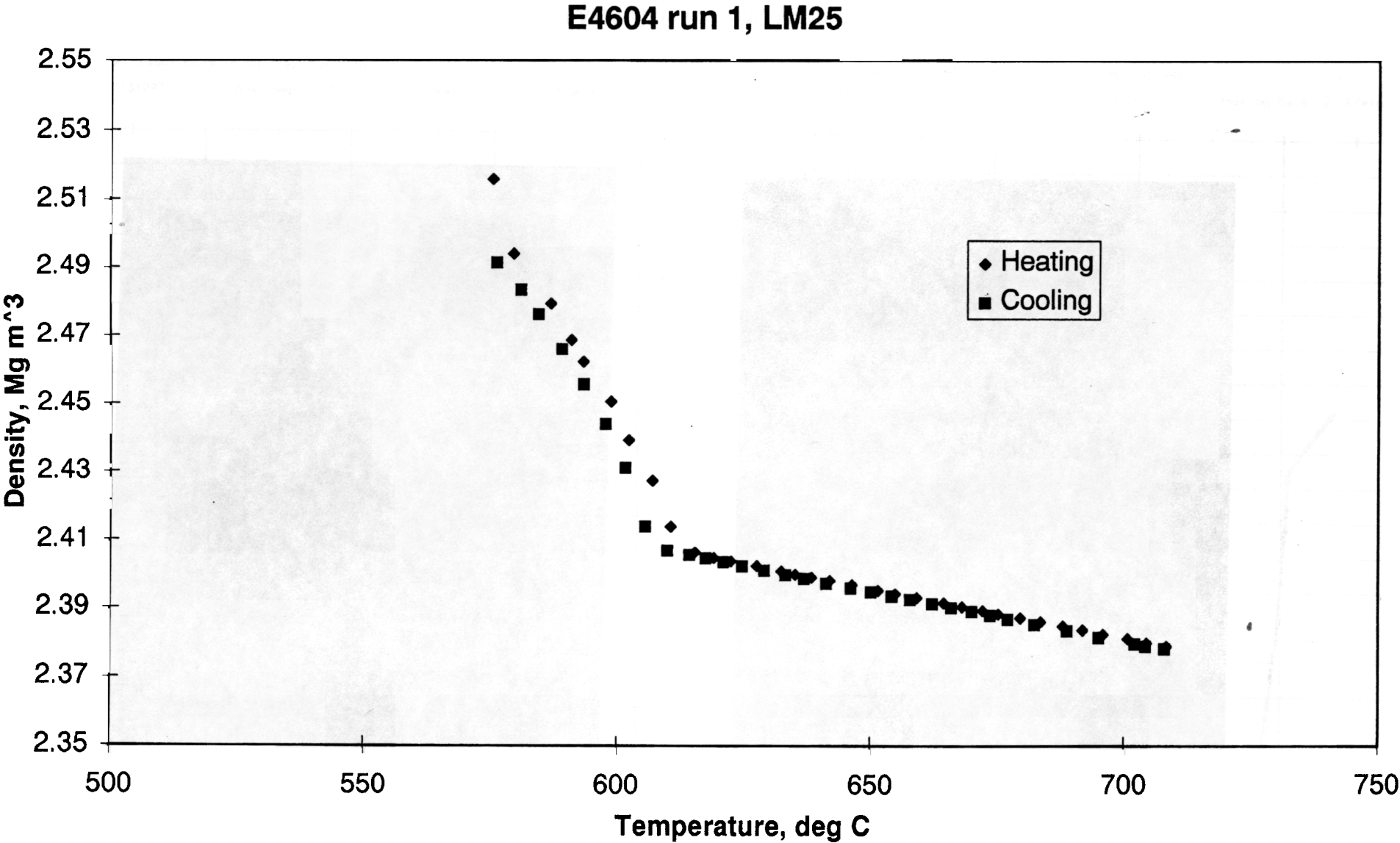


Figure 18 Density as function of temperature for the heating and cooling curves of LM25 estimated using the spreadsheet calculation, showing repeatable behaviour on heating and cooling.

E4604, LM25 run1, melt only

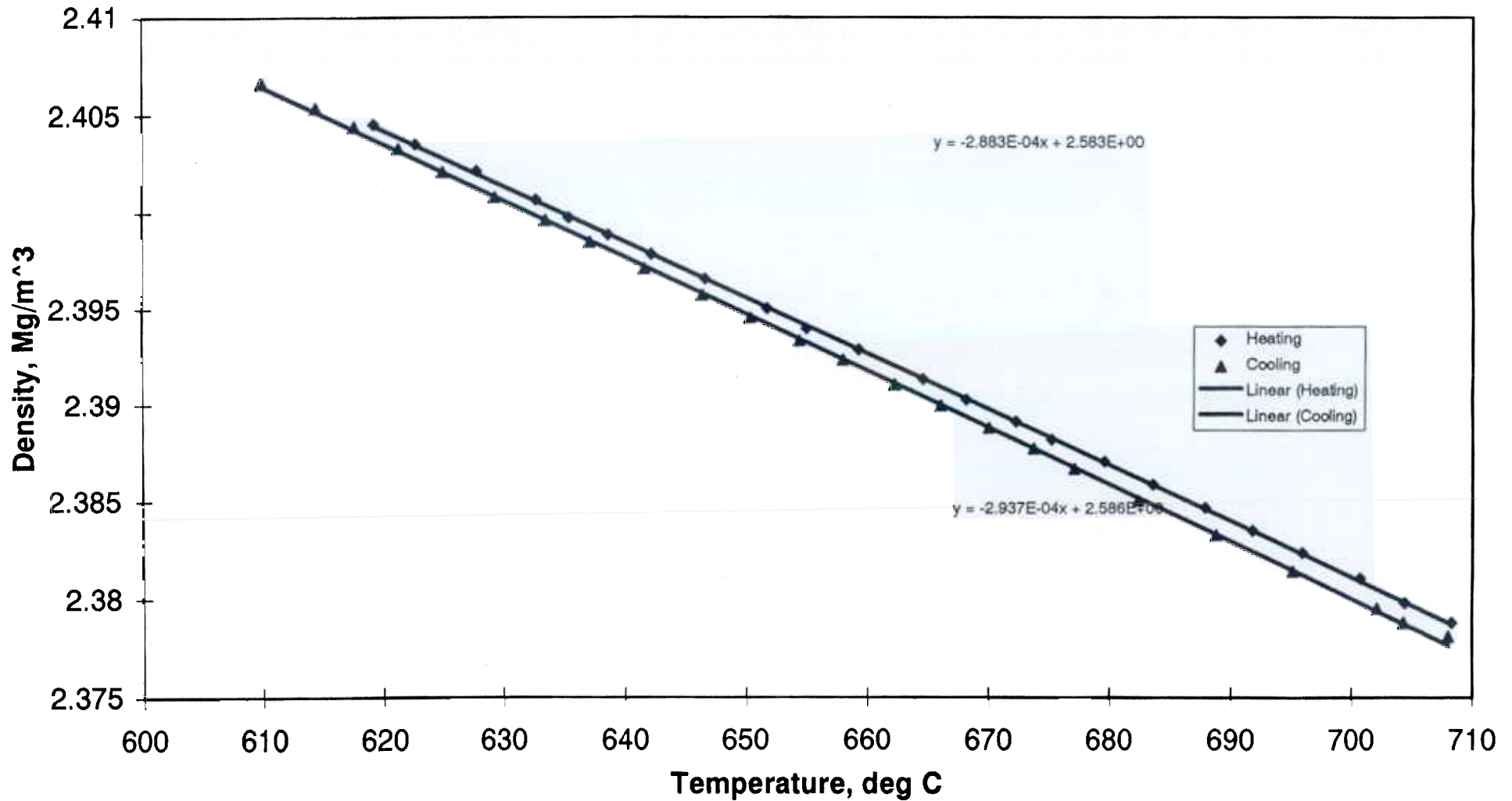


Figure 19 Liquid density as a function of temperature for one thermal cycle on LM25 alloy, with linear regression fits to determine the temperature coefficients.