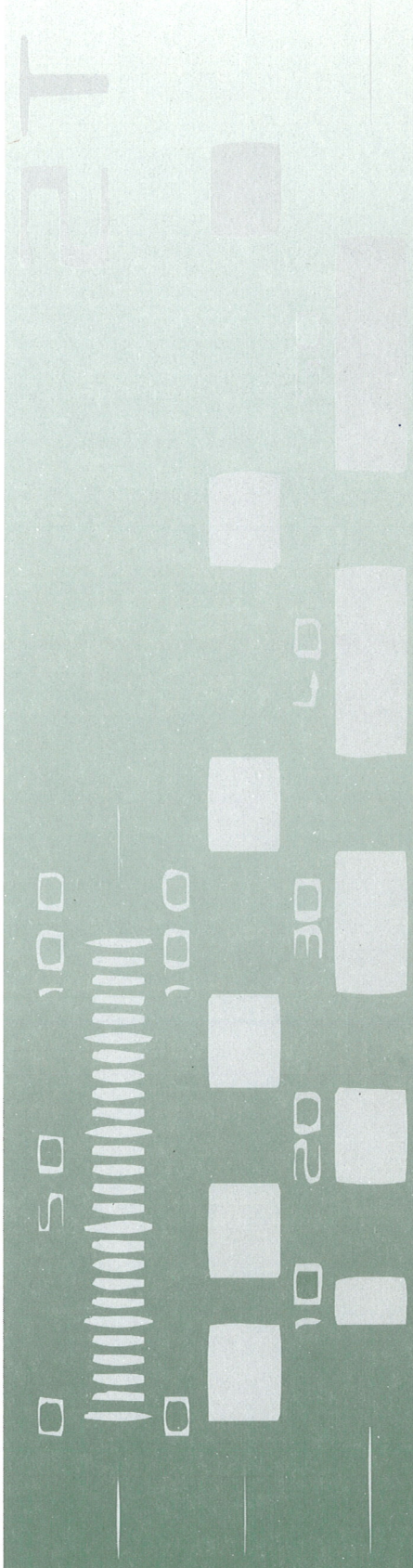
NPL Report CMMT(A)220

REPORT

Feasibility of Measuring Electrical Resistivity up to 1600°C

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January 2000



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Feasibility of Measuring Electrical Resistivity up to 1600°C

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ABSTRACT:

A study was carried out to assess the feasibility of developing an electrical resistivity apparatus capable of measuring the resistivity of liquid metals to a temperature of 1600°C. Details of the four probe electrical resistivity system, associated cleaning system and measurement practice developed are given. Also presented are high temperature resistively measurements made on liquid copper. These measurements were in good agreement with Iida's critically assessed liquid copper resistivity data demonstrating that the new electrical resistivity method is capable of making measurements to 1600°C.

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ISSN 1361-4061

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Approved on behalf of Managing Director, NPL, by Dr C Lea,
Head, Centre for Materials Measurement and Technology

Feasibility of Measuring Electrical Resistivity up to 1600°C

1. Introduction

Process modelling is being increasing used in the casting industry. The driving force for such modelling is improved productivity through lower energy costs, lower scrap losses, improved product quality and product consistency [1]. There are little data available for these models and the data that are available are often of questionable quality. This has been recognised by the Department of Trade and Industry (DTI), who have initiated a number of programmes to improve measurement methods for thermo-physical properties. In the MMP05 Thermal Effects During Solidification of Metallic Alloys project the National Physical Laboratory (NPL) was contracted to develop an apparatus capable of measuring electrical resistivities up to 1100°C in liquid metals (milestone 4). Further to the development of this apparatus, NPL was also contracted to assess the feasibility of extending the measuring capability of the 1100°C electrical resistivity apparatus to 1600°C (milestone 5). This report details T2/M5 the Feasibility of Measuring Electrical Resistivity up to 1600°C. Details of the of the lower temperature apparatus have been reported previously to the DTI and published in an international journal [2]. The method presented here is the high temperature DC four-probe potentiometric method for the measurement of electrical resistivity.

Electrical resistivity is a structure sensitive-property and whilst this property is important in itself, it is the thermal conductivity calculated from electrical resistivity data via the Lorenz relation [3] that are of prime interest to industry. Thermal conductivities calculated from electrical resistivity measurements are often referred to as "indirect" measurements. Where indirect means that the thermal conductivity has been obtained from some property other than temperature.

The thermal conductivity data available for liquid metals have a large uncertainty associated with them[3,4]. Most of these data have been measured using "direct" measurement techniques [3,4]. Where direct means a temperature gradient or temperature response to an energy pulse have been evaluated to obtain a thermal conductivity value. The scatter in the data is a reflection of obstacles faced when making thermal measurements in a liquid metal environment at high temperatures. These obstacles can be summarised as follows:

a. Containment problems at the high temperatures required for metallic systems. It can be difficult to match crucible or measuring probe materials with the metal to ensure there is no chemical reaction.

b. It is difficult to hold liquid metal at high temperatures and make thermal conductivity measurements without there being a convection term associated with the measured value, as thermal instabilities in the measurement systems are enough to initiate convection. This results in an erroneously high thermal conductivity being measured.

c. Thermal conductivity measurements often require the establishing of a temperature gradient on the sample or monitoring of the temperature response of a sample that has been perturbed by an energy pulse. These are difficult conditions to realise experimentally when dealing with liquid metals.

In contrast electrical resistivity measurements are relatively simple, based on Ohm's Law, and are not effected by convection flows. The problem with electrical resistivity calculated thermal conductivities is whether the Lorenz relation is valid for liquid metals and alloys. In a review of thermal conductivity data of pure elements the Lorenz relation was found to be suitable for calculating thermal conductivities from electrical resistivities at the melting point [3]. Also for studies into certain alloy systems [5], notably Cu+Sn, Zn+Al, and Pb+Sn it was also found to hold. For detailed discussion of the Lorenz relation refer to [2,3,5,6].

2. Experimental

As this was a new and very different probe configuration from the previous electrical resistivity set-up [2] there was little by way of an experimental practice to follow prior to the start of this feasibility study. What is outlined in this section is the experimental practice and set-up settled on for the measurements presented and should be viewed as a development in itself. In general, any important issues that were encountered in the development of this practice and set-up will be discussed in Section 3 Instrument Development/Experimental Problems.

The electrical resistivity measurement and software initiation were made in a similar manner to that outlined in the in-house procedure The measurement of Electrical Resistivity of Metals by the Four Probe Method number QPDMM/B/141 that was developed for liquid metals given in Appendix A. The main departures from the existing procedure are outlined below.

2.1. Electrical Resistivity Measurements by the High Temperature DC Four-Probe Potentiometric Technique

Electrical resistivity (ρ) of a metal, is defined in Eq. 1,

$$\rho = \mathrm{R}\cdot\left(\frac{A}{L}\right) \tag{1}$$

where ρ has units Ωm, R is the resistance of the sample in Ω, A is the cross sectional area of the sample in m^2 and L is the distance between the potential measuring electrodes in m. A schematic of the alumina probe developed by NPL to measure the electrical resistivity of liquid metals is given in Figure 1, detailing the L and A term. When measuring electrical resistivity, the measurement volume of the probe, i.e. that defined by the length L and area A, should be at uniform temperature.

In the measurement procedure used by NPL, the A/L term in Eq.1 is not measured directly but calibrated using Hg, a material that is well characterised with respect to

resistivity and temperature. Therefore calibrating at room temperature with Hg gives Eq. 2.

(2) $$\rho_{cal}=R_{cal}\cdot\left(\frac{A}{L}\right)_o$$ at 20°C +/- 0.2°

where the subscript cal denotes calibration and the subscript o denotes room temperature. The resistivity of an unknown sample at room temperature is given by Eq. 3,

(3) $$\rho_{sam}=R_{sam}\cdot\left(\frac{A}{L}\right)_o$$ at 20°C +/- 0.2°

where the subscript sam denotes the unknown sample value.

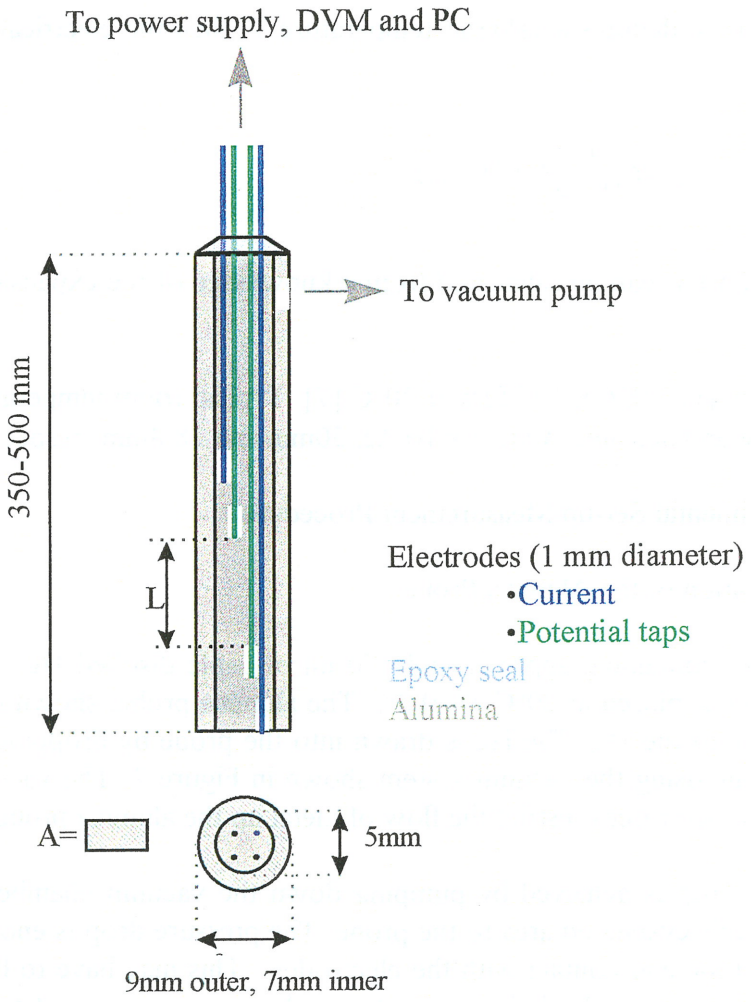


Figure 1. Schematic of the NPL alumina electrical resistivity probe, showing approximate dimensions of the probe.

Rearranging Eq.2 for the $(A/L)_o$ term and substituting into Eq.3 gives,

(4) $$\rho_{sam} = R_{sam} \cdot \left(\frac{\rho_{cal}}{R_{cal}} \right)$$

If the expansion coefficient of the probe material is small and can be considered negligible then Eq.4 is valid for all temperatures. If expansion coefficient is not negligible then the resistivity calculated using Eq. 4 must be corrected for expansion with respect to temperature.

If E, defined in Eq. 5, represents the change in the A/L term with temperature,

(5) $$E = \frac{\left(\frac{A}{L}\right)_T - \left(\frac{A}{L}\right)_o}{\left(\frac{A}{L}\right)_o}$$

where subscript T denotes a value at temperature T, then the electrical resistivity of the sample is

(6) $$\rho_{sam} = R_{sam} \cdot \left(\frac{\rho_{cal}}{R_{cal}} \right) \cdot (1 + E)$$

The value of $(A/L)_T$ can be calculated from a knowledge of the expansion coefficient of alumina.

The value of ρ_{cal} is 0.956×10^{-6} Ωm at 20°C [7]. Typical room temperature values of R_{cal}, L and the annulus area A are $4 \times 10^{-3}\Omega$, 50mm and $18.8mm^2$ respectively.

2.2 Experimental Set-up/Measurement Procedure

2.2.1 Calibration of the Alumina Probe

A glass beaker containing approximately 70 ml of triple distilled Hg is placed in a water bath and stabilised at 20°C +/- 0.2°. The alumina probe, shown in Figure 1, is then inserted into the Hg. The Hg is drawn into the probe by dropping the pressure inside the probe using the vacuum system shown in Figure 2. The vacuum system is required as surface forces restrict the flow of metal up the alumina probe.

The pressure drop is achieved by pumping down the vacuum chamber section and then opening this evacuated area to the probe. The pressure drop is enough to lift the Hg into the probe and contact with the electrodes. This may have to be repeated to fill the measuring area. A platinum resistance thermometer is used to measure the temperature. The electrode material is tungsten. Once the system temperature has stabilised the resistance of the Hg in the probe (R_{cal}) is measured.

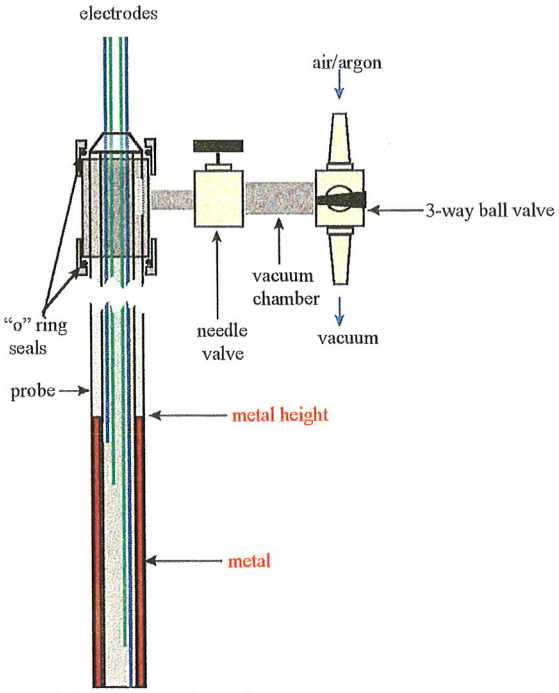


Figure 2. Schematic showing vacuum system used to fill the probe.

This resistance is measured by imposing a voltage on the measuring circuit, measuring the current flowing in the circuit and measuring the voltage drop between the potential taps shown in Figure 1. Each resistance measurement is averaged from two successive resistance measurements (less than 0.5 s apart) where the current polarity is reversed.

The applied current is obtained by measuring the potential drop across a resistor of known resistance, in series with the sample. Fluke 8840 multimeters are used to measure the potential drops. The voltage is imposed on the measuring circuit by a Thurlby power pack, which has a maximum 10 A and 35 V output.

A PC is used to control the power supply, both multimeters, the current relay and also log the measured data. Computer control of the measurement is such that all critical circuit parameters (current, voltage, power on time, temperature measurement step, time measurement step and measurement integration time) can be set on the PC.

Typical values for the voltage drop, the current in the circuit and measured resistance (R_{cal}) for an imposed voltage of 0.5V are 0.3mV, 80mA and 3.8mΩ respectively.

2.2.2 Cleaning of the Calibrated Probe

The Hg must be removed from the calibrated probe prior to using it to make a measurement. In the lower temperature apparatus this was a simple process [2] were the electrodes could be removed from the silica cell and wiped clean. The silica cell would then be dipped in nitric acid to dissolve away the Hg. In the alumina cell the tungsten electrodes are fixed and sealed to the alumina and cannot be removed. Also, nitric acid oxidises tungsten, therefore the alumina cannot be dipped in the acid.

To overcome this problem the apparatus, shown in Figure 3, was developed to remove the Hg. This apparatus exploits the high vapour pressure associated with Hg [7]. The probe, sealed in a pyrex tube, is heated to approximately 90°C in a resistively heated Cu block. Simultaneously, the pyrex tube is evacuated. The raised temperature and the low pressure favours the evaporation of Hg. The gaseous Hg is condensed and collected in the liquid nitrogen cold trap, shown in Figure 3. Closing the ground glass valves allows the condensed Hg to be isolated and removed from the apparatus. After removal of the Hg, the probe is ready to be used for a measurement.

The whole apparatus is mounted on a trolley. For safety reasons, when in use, it is encased in a perspex shield and vented via ducting to the laboratory gas extraction system.

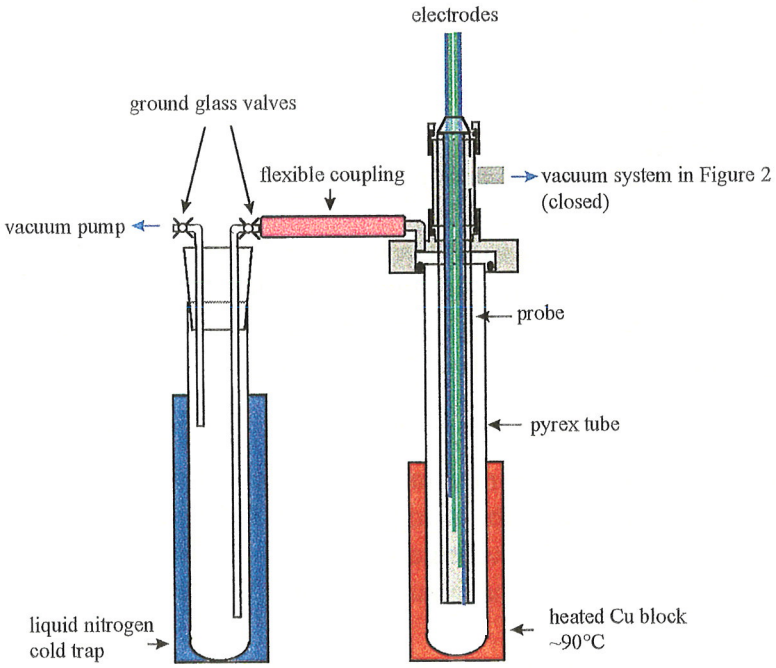


Figure 3. Schematic of the Hg removal apparatus

2.2.3 Making a Measurement Using the Calibrated Probe

2.2.3.1 Positioning of the Calibrated Probe in the Furnace

A schematic of the experimental set-up is given in Figure 4, where the probe shown in Figure 1 is fixed and sealed to the top stainless steel plate centred on the vertical axis of the platinum furnace. The crucible plus sample are initially situated just below the bottom of the alumina probe. The furnace is then heated to the required temperature. This temperature must be greater than the melting point or liquidus of the metal. Once molten the crucible plus sample are then raised to make contact with the probe. Care must be taken to ensure that the crucible is not raised so high that the crucible bottom comes in contact with the probe. Therefore knowledge of the crucible and

probe positions prior to raising the crucible and the distance the crucible is raised are critical. The position of the crucible and probe prior to raising the crucible are measured when setting up the equipment.

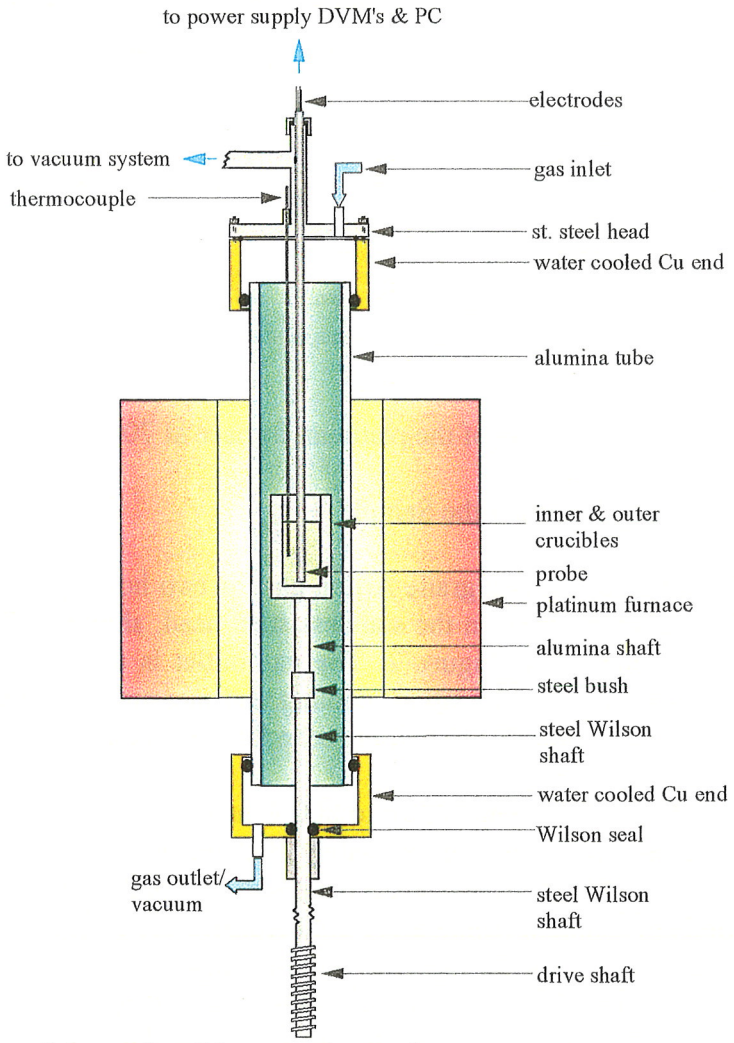


Figure 4. Schematic of the experimental set-up

There is a ruler attacked to the furnace support and marker attached the drive shaft (shown in Figure 4) to measure the travel of the drive shaft and hence the height raised by the crucible.

Both the crucible (70mm) and the measuring part of the probe (60mm) must be positioned in the hot zone of the furnace. Also to ensure that the probe is not thermally shocked when the liquid metal is drawn into the probe using the vacuum system in Figure 2, a minimum of a further 20mm on top of the measuring part of the probe must be positioned in the hot zone. The requirements are such that the furnace must have hot zone of length approximately 150mm. This is not a trivial requirement and is considered a design constraint on the apparatus.

A example of the temperature profile through the platinum furnace at 700°C is given in Figure 5. The hatched area is the hot zone.

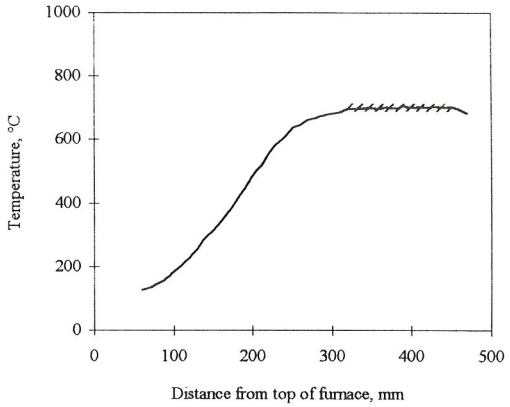


Figure 5. Temperature profile of the platinum furnace at 700°C.

2.2.3.2 Purging and Heating the Sample

The furnace is purged with research grade Argon gas for two hours prior to heating. Gas enters the furnace at the inlet on the stainless steel head, shown in Figure 4 and through the probe as marked on Figure 2. The gas outlet is at the bottom of the furnace as marked in Figure 4. All heating, cooling and measurement operations are carried out under Argon. In general the melting schedule was as follows:

Heat from room temperature to 800°C at 10°/minute
Dwell time at 800°C approximately 30 minutes
Heat from 800°C to maximum temperature required at 5°/minute
Hold at maximum temperature until temperature stabiles
Close off gas flow through the alumina probe
Raise the crucible to immerse the alumina probe in the metal,
Draw the metal up the alumina probe so that the metal makes contact with the electrodes
Measure the electrical resistivity
*Cool to required temperature at between 1 and 5°/minute
*Hold at required temperature until temperature stabiles
*Measure the electrical resistivity
For further measurement cool/heat as asterisked above
If measurement complete shutdown equipment

2.2.3.3 Measuring the Resistivity of the Liquid Metal

The cleaned calibrated probe is placed in the platinum furnace as shown Figure 3. As with Hg in the calibration run, the liquid metal is drawn into the probe by dropping the pressure inside the probe using the vacuum system shown in Figure 2. The temperature is measured using a Pt/Pt13%Rh thermocouple. Once the system temperature has stabilised the resistance of the liquid metal in the probe (R_{sam}) is measured. The method of measuring the resistance is the same as was outlined in

section 2.2.1 when calibrating using Hg. Resistivity values are obtained by the use of Eq. 4. Corrections for expansion are carried out separately on a spreadsheet using Eq. 6. The data used for the expansion correction are from Touloukian [8] and are discussed later.

As before, computer control of the measurement is such that all critical circuit parameters can be set on the PC. The resistivity calculation requires manual input of the R_{cal} value measured when calibrating the probe outlined in section 2.2.1. The resistivity measurements can be made at either constant temperature or time intervals.

2.2.4 Correction for Expansion of the Alumina Probe

Alumina is an anisotropic material. It's expansion behaviour as reported in Touloukian [8] is given in Table 1, where l_o is the length at 20°C, Δl is the change in length in heating/cooling from 20°C and // denotes parallel to.

	$\%\Delta l/l_o$	$\%\Delta l/l_o$	$\%\Delta l/l_o$
T,°C	//c-axis	//a-axis	polycrystalline
-173	-0.078	-0.060	-0.066
-123	-0.060	-0.047	-0.051
-73	-0.041	-0.037	-0.038
-23	-0.020	-0.023	-0.022
20	0.000	0.000	0.000
127	0.078	0.074	0.074
227	0.155	0.146	0.147
327	0.236	0.221	0.224
427	0.320	0.300	0.305
527	0.408	0.382	0.389
627	0.499	0.466	0.476
727	0.593	0.554	0.566
827	0.690	0.644	0.658
927	0.790	0.737	0.754
1027	0.892	0.832	0.851
1127	0.997	0.929	0.951
1227	1.105	1.028	1.053
1327	1.214	1.128	1.157
1427	1.326	1.231	1.263
1527	1.440	1.334	1.370
1627	1.556	1.439	1.478

Table 1. Expansion data for alumina from Touloukian [8]

To assess the effects of expansion and anisotropy of the alumina on the (A/L) term calculations of the % change of (A/L), and hence from Eq. 1 change in ρ, of a sample for different expansion conditions with temperature were made. Calculations of the change in (A/L) for the following three different expansion conditions are given in Figure 6.

i. **Effective isotropic**, where the polycrystalline expansion data in Table 1 is used to calculate the probes expansion behaviour.

ii. **Anisotropic**, the annulus area expands parallel to the c-axis and the length expands parallel to the a-axis.

iii. **Anisotropic**, the annulus area expands parallel to the a-axis and the length expands parallel to the c-axis.

The expansion effects were calculated for typical probe dimensions where L=50mm, the outer diameter of the 4-bore tube is 5mm and inner diameter of the cell wall is 7mm.

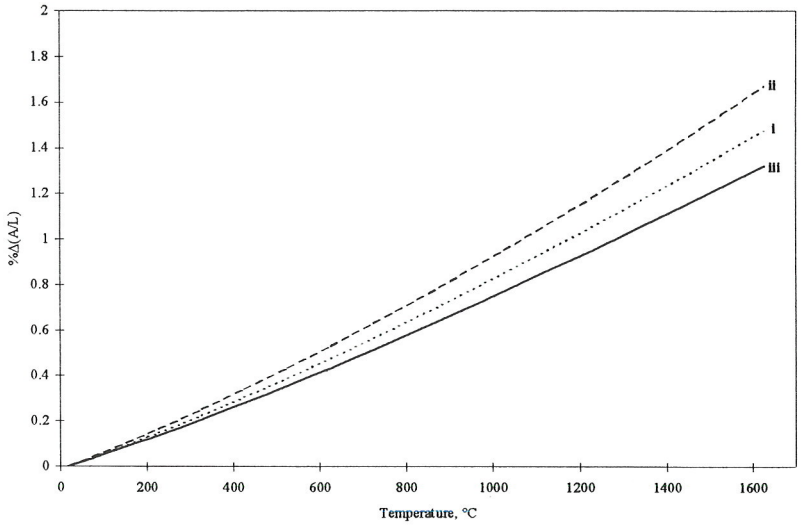


Figure 6. % change in (A/L) value for different expansion conditions.

From Figure 6 it can be seen the corrections to the (A/L) term are small and that ii represents the largest expansion correction. At the highest temperature of 1627°C the corrections of i, ii and iii are 1.48, 1.67 and 1.32 % respectively. At moderate temperatures, for relatively benign materials such as Cu, where expansion of the probe is not an issue, the uncertainty in the measurement is estimated to be 1.7% [2]. Given this uncertainty, the difference between the (A/L) corrections for different expansion coefficients is negligible. As the correction values are of a similar order to that of the uncertainty, the measured electrical resistivity values should be corrected for expansion. The alumina material used for the probe is polycrystalline and is best represented by curve i. As such, all resistivity measurements presented will be corrected for expansion using the polycrystalline data and Eq. 6.

3. Instrument Development/Experimental Problems

3.1 Cell Design

The original cell design for measuring liquid metals was based on a silica electrical resistivity probe shown in Figure 7. This probe was easy to manufacture, robust, easy to use, easy to clean (see section 2.2.2) and had a very small expansion coefficient. Unfortunately silica has a softening temperature somewhere between 1100°C to

1200°C. It is therefore not suitable for use at temperatures up to 1600°C.

The probe material chosen for these higher temperatures was alumina. This material was chosen because, it has good high temperature chemical and physical stability characteristics and it is readily available in a number of different shapes and sizes.

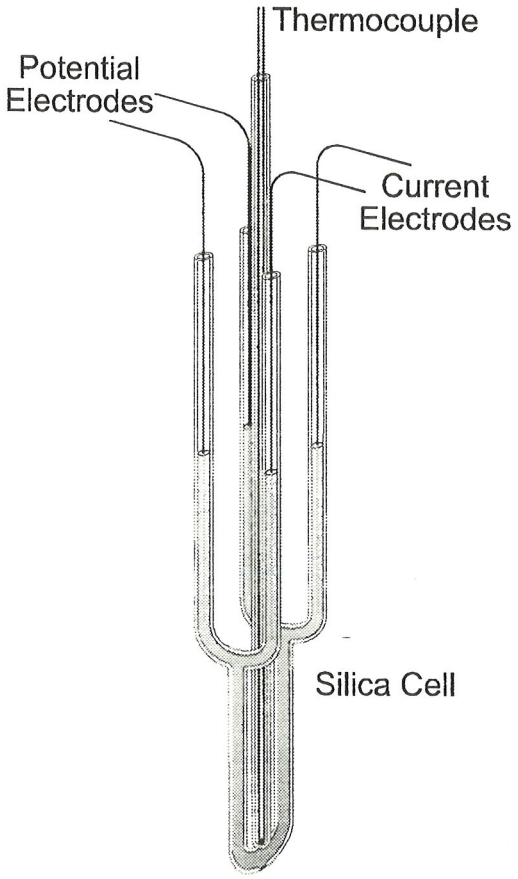


Figure 7. Schematic of the silica probe.

The disadvantages were that it was not easily machined or produced to a complex geometry, it had a significant expansion coefficient and was known to start electrically conducting at high temperatures [9]. These disadvantages could be minimised by appropriate design and a knowledge of the expansion and electrical properties of alumina.

It was envisaged that the alumina probe would be a consumable i.e. not survive the electrical resistivity measurement. Therefore where possible to minimise the cost of each alumina probe, it would be designed around standard readily available alumina parts.

3.1.1 Cell Geometry

The initial alumina cell design was similar to that shown in Figure 1 and is given in

Figure 8. The main differences from the initial alumina cell design were in the size of the probe and the position of the electrodes. The initial cell design was smaller, CF lengths of 300mm with 350-500mm, and the distance between the potential taps was shorter, CF 30mm with 50mm. Also, the relative position between the potential tap and current electrode changed. In the original probe, as shown in Figure 8 the current electrode was positioned at the beginning of the opening for the potential tap.

In Figure 1, there is a gap of approximately 2.5 mm.

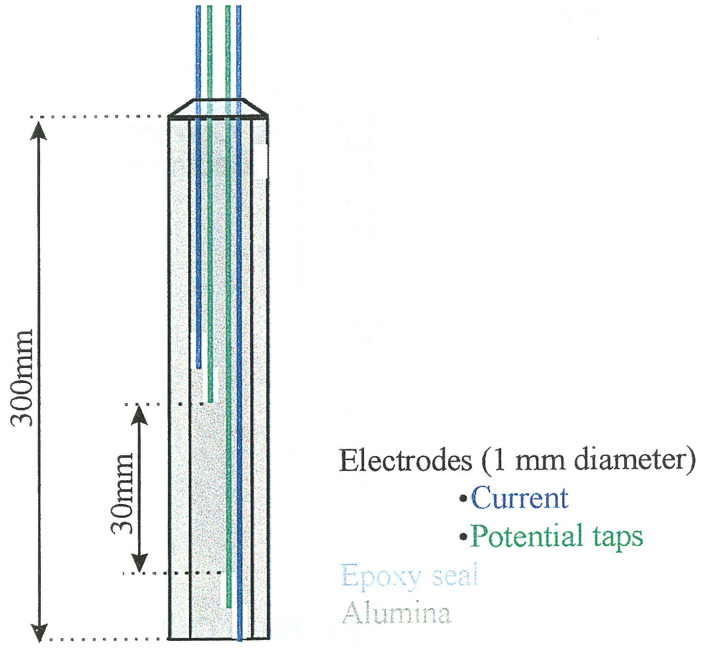


Figure 8. Schematic of the original alumina electrical resistivity probe.

The change in overall length of the probe was principally due to a changes required to place the probe the hot zone of a new high temperature furnace, but also reflected experimental constraints of temperature stability of the measurement and thermal shock problems when using the probe. The original furnace's hot zone was smaller than that required for measurement using the alumina probe and had to be replaced.

As mentioned previously in section 2.1 the measuring part of the probe, (which is approximately 60 mm long) should be at uniform temperature when making a measurement. To be at uniform temperature when making a measurement the measuring part of the probe must be wholly located within the furnace hot zone.

Drawing liquid metal into areas of the probe that were significantly lower in temperature than the melt caused thermal shock problems. In Figure 5, it can be seen that the temperature of the furnace drops off rapidly at distances away from the hot zone. To minimise the risk of drawing metal into the low temperature area the probe was positioned approximately 20mm deeper into the hot zone than was required for the measuring part of the probe alone.

3.1.2 Positioning of Electrodes

The position of the electrodes is important when considering the error associated with a resistivity measurement. The error associated with the position of the electrodes is a reflection of the signal to noise ratio in the measurement of the potential drop between the potential taps. There are two ways to improve the signal to noise ratio. Lower the amount of electrical noise or increase the signal voltage. Electrical noise can have many sources such as stray electrical fields from other equipment, small variances in the mains supply, junction contacts etc., it is difficult to effect much control over these sources. Increasing the voltage signal i.e. the potential drop across the sample is more practical. The potential drop voltage can be increased by either

a. increasing the imposed voltage on the circuit or
b. minimising the A/L value of the probe.

For a given resistance, an increase in circuit voltage would increase the power by the voltage squared. This increase in power could result in the heating of the liquid metal and is to be avoided. Also, the high voltages may change the electrode surface properties to a degree that the calibration may no longer be valid.

The potential drop in the circuit can be to some degree controlled by varying the (A/L) term in Eq.1. For a given resistivity, minimising this term increases the measured resistance of the sample. For a constant current I, where V=IR, the potential drop between the potential taps in the probe must also increase.

Generally when measuring resistivity it is preferred to work at low circuit voltages and increase the measured resistance via control of the (A/L) term [6,10].

Attempts to reduce the area A shown in Figure 1 by using different diameter tubing failed, as it proved very difficult to draw the liquid metal into the probe uniformly. This resulted in asymmetric and therefore undefined filling of the probe.

More success was achieved by increasing the distance between the potential taps from 30mm to approximately 50mm. This increased the measured resistance by almost 80%. The original length was at least in part defined by the length of the hot zone of the furnace. Increasing the distance between the samples increased the size of the hot zone required for the measurement. This increase in distance coupled with the thermal shock problems outlined previously, meant that the original furnace had to be replaced with one that had longer hot zone.

There was some concern over the relative position of the current and potential electrodes in the original probe design. As the current electrode was very close to the potential electrode, it was possible that the potential drop measurement was being made in an asymmetric part of the current field. To address this problem the current and potential electrodes where set apart, as shown in Figure 1, by approximately 2.5 to 5mm.

3.2 Furnace/Equipment Adaptations

The following adaptations were made to the furnace set-up in order for it to operate successfully at 1600°C, most of which are shown on Figure 4.

a. The silica work tube was replaced by alumina (see Figure 4).
b. The furnace head had to redesigned to accommodate and hold the new probe and thermocouple configuration.
c. In the original configuration the steel Wilson shaft had a small alumina rod attached to it's top end to protect it from the high temperatures of the hot zone. The length of this alumina shaft had to be increased to ensure the steel shaft was not exposed to too great a temperature.
d. A radiation shield (not shown in Figure 1) was placed at the steel bush to reduce heat losses down the tube and to protect the Wilson seal from metal spillage.
e. Due to the sample volume requirement and the smaller inner diameter of the furnace tube non-standard crucibles had to be made.
f. An extra gas line and valve was added to the system to purge the internal volume of the alumina probe (discussed in section 3.3.2).

Also as mentioned previously, because of the hot zone length requirement the furnace had to be replaced and refitted.

3.3 Oxidation of Electrodes

3.3.1 Oxidation of Electrodes by Nitric Acid

In the initial stages of design of the new probe oxidation of the electrodes was considered a major problem. The reason being that the tungsten electrodes were expected to react with the nitric acid used to clean away the Hg (discussed fully in section 2.2.2). If so this would change the electrical properties of the tungsten electrode surface and invalidate the Hg calibration.

To test whether the tungsten electrodes would oxidise in nitric acid the resistance between two tungsten electrodes in a Hg bath where measured before and after steeping in nitric acid for 10 minutes. The temperature, depth of immersion, depth of Hg and position in the Hg bath where the same before and after steeping in nitric acid. The resistance increased from 0.005 to 0.0012Ω's after dipping in nitric. Thus confirming that the electrodes resistance did change. This problem was successfully overcome by the cleaning apparatus as described in section 2.2.2.

3.3.1 Oxidation of Electrodes by Furnace Atmosphere

To ensure that the furnace, sample and probe were heated up in a neutral atmosphere the furnace was purged with research grade argon for two hours prior to heating. The original gas flow circuit was through the gas inlet at the top of the furnace and out through the bottom of the furnace as shown on Figure 4. Under such conditions it

was found that the electrodes were oxidising and any attempt at measuring the electrical resistivity of a liquid metal at high temperatures failed. It was unclear what was causing the oxidation. Possible reasons for the oxidation of the tungsten electrodes were

a. the oxygen potential in the research argon atmosphere is high enough to cause significant oxidation,
b. there was a leak in the furnace probe system causing oxidation or
c. the probe area A, as shown on Figure 1, was not being purged of air.

The tungsten used for the electrodes suffered no observable oxidation effects when used in other applications in similar atmospheres at high temperatures. Therefore it was unlikely that the oxygen associated with the argon gas is responsible for the electrode oxidation.

To test 'c' the probe area A not being purged of air, an argon line was attached the vacuum system's three way valve as shown on Figure 2. On heating up, the three way valve and needle valve the were open to the gas line. Gas now flowed into the furnace both through the gas inlet marked on Figure 1 and the vacuum system shown in Figure 2. This gas flow set-up eliminated the electrode oxidation problem. It was therefore concluded that 'c' the probe area A was not being purged of air. Heating up procedures were adapted accordingly.

4. Results/Discussion

To assess the resistivity measurement performance of the NPL high temperature alumina probe measurements where made on pure copper. The results are shown in Figures 9 and 10. These data were compared with Iida's recommended values [6] as measured by Kita et al [10] and Roll and Motz [11]. Measurements where also made on this material using the silica low temperature probe [2]. The silica probe measurements were in good agreement with the recommended values, the differences from Kita [10] and Roll and Motz [11] being approximately 1% and <<1% respectively. For all intents and purposes the silica probe data can be represented by the Motz values [11] and have not been included in Figures 9 and 10. The scatter in Kita et al's [10] and the silica probe data [2] was of the order +/-2% and +/-1.5% respectively. From the Motz [11] paper it was impossible to assess the scatter in the data but it is unlikely to be any better than that of Kita [10] and therefore is assumed to be at best of the order of +/-2%. The Kita [10] method was an alumina four probe set-up.

The Cu was heated to approximately 1200°C, cooled to just above the melting point then heated to the maximum temperature achieved in the experiment. Measurements were made as follows:

a. Cooling from the liquid and stabilising the temperature for 15 minutes denoted static.
b. Cooling from the liquid at a cooling rate of approximately 1°C per minute

while making measurements denoted cooling.

c. Heating from just above the melting point at approximately 1°C per minute while making measurements, denoted heating.

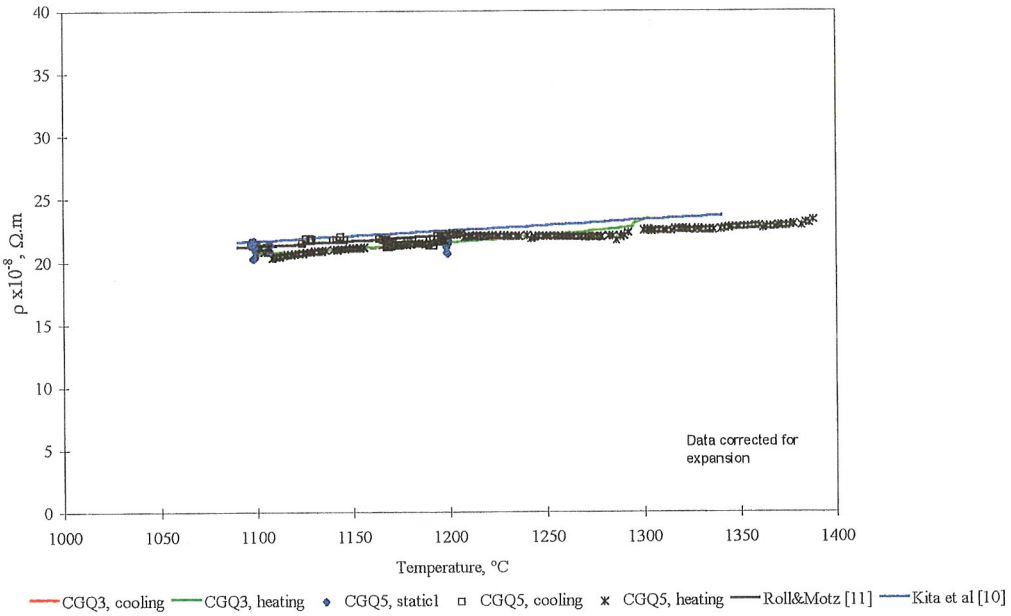


Figure 9. Copper resistivity versus temperature, coarse scale.

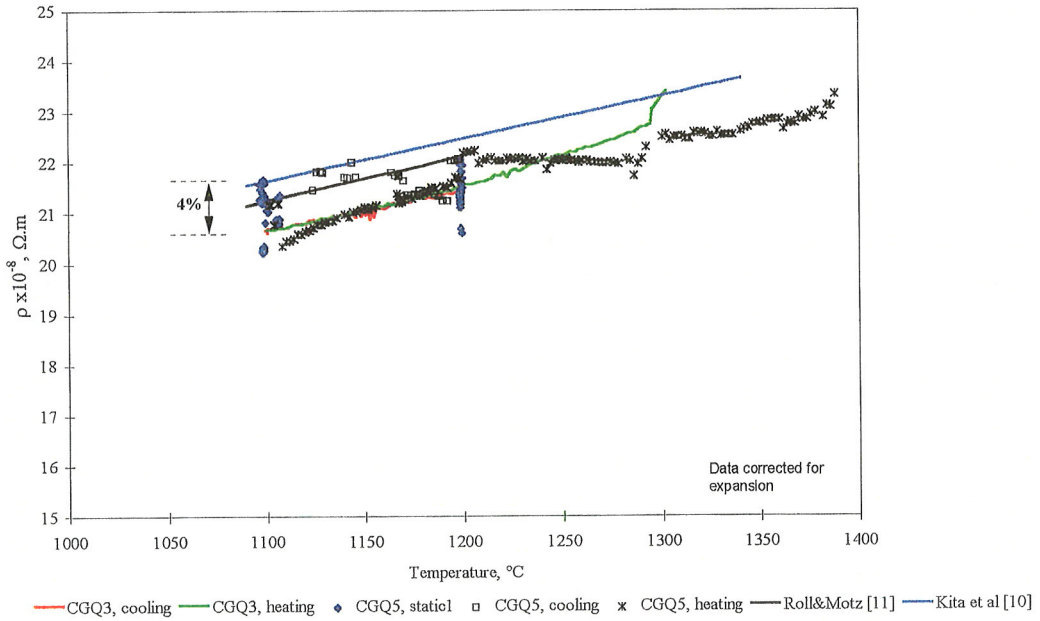


Figure 10. Copper resistivity versus temperature, sensitive scale

In Figure 9 it can be seen that the NPL alumina probe resistivity measurements of Cu are marginally lower than the Motz [11] and Kita [10] values. The approximate differences in the measurements, based on mean values at a given temperature, and the recommended values are between 1 and 4% and 0 and 3% for the Kita [10] and Motz [11] data respectively. The temperature coefficient of the NPL alumina probe resistivity data is, within the scatter of the data, the same as that of the recommended data. The maximum temperature the NPL alumina probe reached was approximately

1400°C. Figure 10 enables viewing of the data in more detail. The sudden rise of CGQ3 at ~1300°C, shown in Figure 10, was due to an experimental problem that damaged the alumina probe. The step in the CGQ5 results is coincident with the raising of the liquid metal level using the vacuum system in Figure 2. The scatter in NPL alumina probe data, best shown in Figure 10, is approximately +/-3%.

Considering the respective scatter on all the data, it can be argued that there is reasonable agreement with all the resistivity values shown in Figures 9 and 10. The lower limits in the scatter of recommended data overlap with the upper limits of the NPL alumina probe data. The mean resistivity of Cu from the data shown in Figures 9 and 10 lies somewhere slightly below that of the Motz [11] line on the graphs. The fact that the values measured by the NPL alumina probe are reasonable agreement with the recommended values can be considered as evidence that probe is capable of making resistivity measurements at high temperatures.

The scatter in the alumina probe resistivity measurements is similar but slightly higher than that reported by Kita [10] but greater than that of the silica probe [2]. This increased scatter is likely to be a result of the different geometries used in the Kita [10], NPL silica [2] and alumina probes.

The geometry of the silica probe was better suited to make resistivity measurements. Unfortunately it is extremely difficult to duplicate such a geometry in alumina. Approximate values of (A/L) for the Kita [10], silica[2] and the NPL alumina probes are 0.12mm, 0.03mm and 0.4mm respectively. The larger the (A/L) the greater the uncertainty associated with the measurement as a result of a poorer signal to noise ratio (as discussed in section 3.1.2). Therefore the increased scatter in the NPL alumina probe measurements is as expected.

It is more difficult to explain the lower resistivity values of the NPL alumina probe. There are a number of possible explanations for this behaviour.

a. The effects of expansion in the alumina probe are not being accounted for properly.
b. The properties of the electrodes are changing in some manner that affects the resistivity measurement.
c. Composition differences in the material measured.
d. Bubble formation in the measurement cell.
e. The electrical conductivity of the alumina causing an underestimation of the measured resistivity value.

It is unlikely a through to c are responsible for the low NPL alumina probe resistivity measurements.

The expansion of the NPL alumina probe was discussed in section 2.2.4. It was shown there that under even the worst conditions where the probe was expanding in an anisotropic manner the error would only be as great as 1.67 % 1600°C. This is

approximately 0.1% different from the polycrystalline expansion correction that is applied to the data. A 0.1% difference can be considered negligible with respect to the observed differences in the data. It is likely that Kita et al [10] took a similar approach to the expansion of alumina but it is not clear from their paper how they corrected for expansion or what expansion data they used.

The effect of the electrodes and sample material composition can also be discounted. As the same electrode and copper materials were used for both the NPL silica [2] and NPL alumina probe measurements.

The effects of bubble formation and the electrical conductivity may offer some explanation as to why the NPL alumina probe resistivity results are lower.

4.1 Bubble Formation

Two types of bubble formation must be considered.

a. A bubble that forms and completely blocks the conduction path.
b. A bubble that forms and partially blocks the conduction path.

If the bubble that forms completely blocks the conduction path, it will register as an electrical break in the circuit (infinite resistance) and is easily recognised. If the bubble only partially blocks the conduction path then a high (apparent) resistivity will be measured. This is a result of a change in A, the cross sectional area, of the (A/L) term. It is difficult to detect or identify such bubble formation. Also, once a bubble is formed in the measurement area it is difficult to remove it. In ambient temperature systems the measurement cell would be agitated/vibrated to aid the removal of the bubble but this is more difficult in high temperature systems. Agitation of the higher temperature probes (Kita [10], Motz[11], NPL silica [2] and alumina) is difficult due to restrictions of access (the probe is contained in a furnace) and the brittle nature of the probe materials (ceramic/glass).

It is also possible to remove bubbles from a liquid metal by reducing the atmospheric pressure above the liquid metal. Unfortunately the designs for the Kita [10], Motz [11] and silica probe [2] did not include such a provision. With the NPL alumina probe it was possible to lower the pressure above the liquid metal in the probe using the vacuum system in Figure 2. Therefore the NPL alumina probe measurements should be less susceptible to bubble formation problems.

4.2 Alumina Electrical Conductivity

To assess the possible effects of the conductivity of alumina on the resistivity measurement the following calculations were carried out.

The resistivity measurement cell was considered as three resistors in parallel as shown in Figure 11,

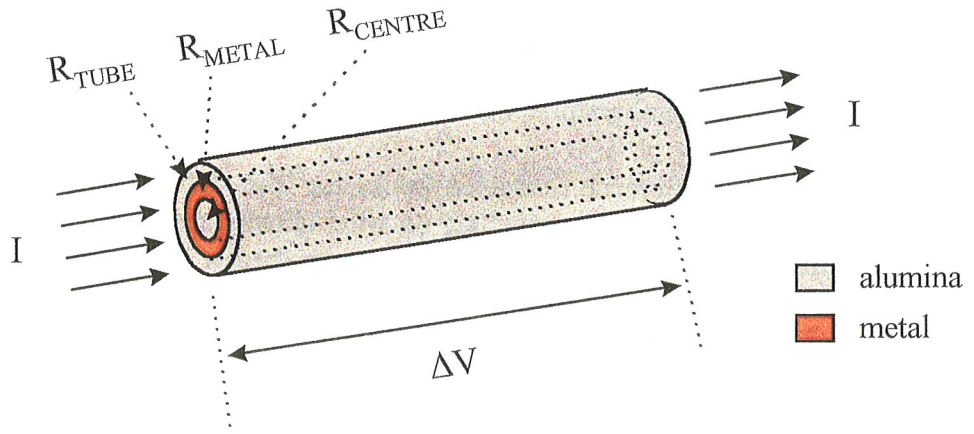


Figure 11. Schematic of the resistor circuit.

where, R denotes resistance of the materials, I is current in the circuit, and ΔV is the potential drop across the measuring part of the probe.

For such a circuit the measured resistance in the probe (R_{PROBE}) is given by Eq. 7.

(7) $$\frac{1}{R_{PROBE}} = \frac{1}{R_{TUBE}} + \frac{1}{R_{METAL}} + \frac{1}{R_{CENTRE}}$$

Rearranging Eq. 7 for the resistance of the metal (R_{METAL}).

(8) $$\frac{1}{R_{METAL}} = \frac{1}{R_{PROBE}} - \left(\frac{1}{R_{TUBE}} + \frac{1}{R_{CENTRE}} \right)$$

Using resistivity data from the alumina suppliers datasheet [12] and Morrell's ceramic handbook [9], given in Table 2, the % change in the measured resistancies, as defined in Eq. 9, were calculated for a standard probe geometry and representative resistance values for Cu. These % differences are also given in Table 2.

(9) $$\%Diff = \frac{(R_{METAL} - R_{PROBE})}{R_{PROBE}} \times 100$$

Temperature, °C	Alumina resistivity, Ωm (datasheet [12])	% Diff	Temperature, °C	Alumina resistivity, Ωm (Morrell [9])	% Diff
1000	1×10^5	0.0007	1000	1×10^4	0.007
1500	1×10^2	0.82	1200	1×10^2	0.74
-	-	-	1400	5.62×10	1.40
-	-	-	1600	1.78×10^{-1}	4.99

Table 2. Alumina resistivity data and calculated % difference resistivity data.

The resistance calculations where based on an initial room temperature probe geometry with centre diameter of 5mm, metal annulus thickness of 1mm, a tube thickness of 1mm and a cell length of 50 mm. These values where then corrected for expansion due to temperature using the polycrystalline data in Table 1. The assumed measured resistance values (R_{PROBE}) where varied linearly with temperature between 0.00075 Ω and 0.00093 Ω for temperatures 1000°C and 1600°C respectively.

The consequences of the % difference resistance values for the real as opposed to measured resistivity value are different depending on what alumina resistivity data is used. When using the values from the alumina suppliers data sheet it can be seen that over the temperature range 1000°C to 1500°C the effect is minimal. Even at 1500°C a correction of only 0.82% is required on the resistance and therefore from Eq. 1 the resistivity. This is much smaller than the scatter in the data and is therefore negligible.

If using the data from Morrell [9] then the resistivity correction may be significant. The measured resistivity values would be too low and therefore would have to be corrected "up". This would reduce the discrepancy between the measured values in this study and those of Kita et al [10] and Motz et al [11]. Although at 1400°C this correction would still only be 1.4%.

It is not clear which alumina resistivity data is most appropriate when correcting the metal resistivity. It is likely that the data on the manufacturers datasheet can only be considered an indication of the materials behaviour. On the other hand it is difficult to know exactly what data to use from Morrell's handbook [9]. The resistivity values change by orders of magnitude depending on what the impurity level of the alumina. The values used in this report are what were considered most representative of the alumina material used in the NPL alumina probe. There is no easy way of knowing what data are most suitable without having the alumina material's resistivity measured. Also it is unlikely that the Kita et al [10] corrected for the conduction of alumina in their measurements. Therefore it is unclear how much the NPL alumina probe's resistivity and Kita's values would converge should a correction be applied. This convergence (or divergence) would be dependent on the resistivity properties of both alumina probes.

Regardless of which resistivity values are used, the effect of the alumina resistivity does not fully explain the differences between the NPL alumina probe measurements and the recommended values.

4.3 General

The developments of the NPL alumina probe are such that it is capable of measuring liquid metals up to temperatures of 1600°C. In principle the NPL alumina probe can be used to temperatures up to around 1700°C. The temperature capability of the probe has been demonstrated by measuring liquid Cu to high temperatures and

obtaining resistivity data comparable to the recommended Cu resistivity values [6]. Further, the vacuum apparatus used for drawing the liquid metal into the probe enables some control over removal of bubbles that may form in the measurement cell. The principle limitations of the probe are threefold.

a. The softening of the alumina probe material at very high temperatures (approximately 1700°C) invalidating the probe calibration.
b. The electrical conductivity of the alumina becoming so high at high temperatures that the measured resistance obtained by the probe will be too small.
c. Matching electrode composition to the resistivity sample to minimise reaction between the two.

The upper temperature working limit will ultimately be decided by "a", as a change in probe geometry at high temperatures would be difficult to control. To some degree "b" can be controlled if the alumina material used in the probe is of a higher quality and better characterised with respect to it's resistivity. The electrode composition effect "c" is more difficult as there may not always be a suitable electrode material available for the liquid metal alloy you want to measure. It may be possible to overcome this problem by using electrodes made of the parent metal of the alloy of interest. Such measurements are only likely to be possible over a limited temperature range and for a limited measurement time.

Also for pure materials it is possible to use the metal of interest as the electrode material. At liquid metal measurement temperatures the electrode would be both solid and liquid. Care would have to be taken to develop a suitable measurement practice as it is likely that these measurements could only be made on a heating cycle. Cooling would have the effect on contracting the liquid metal part of electrode away from the solid part.

5. Conclusions

a. A high temperature electrical resistivity apparatus and probe has been developed that is capable of measuring to above 1600°C. The apparatus consists of an environmental chamber (placed in a furnace), an alumina probe (connected to the appropriate electronics) and a vacuum system capable of systematically filling the probe.

b. The system is capable of measuring resistivities to within 3% of the recommended values of Cu and is less susceptible to bubble formation problems during measurement than other apparatus.

c. A cleaning system, to clean the probe has been developed that enables safe removal of Hg from the probe without damaging the probe electrodes.

d. Calculations of the expansion effects for the alumina probe have shown that even at high temperatures the expansion corrections for the resistivity measurements

are small and anisotropic expansion effects on the measurement are negligible.

e. The effect of electrical conduction of the alumina on the measurement of electrical resistivity of the metal at high temperature could effect the resistivity measurement. The size of this effect was dependent on the particular conductivity of an alumina material. This in turn was highly dependent on the grade of alumina used in the probe.

6. Recommendations

a. The probe design should be further developed to optimise the (A/L) to reduce the uncertainty in the resistivity measurements.

b. The electrical resistivity of the alumina probe material used to make the probe should be better characterised. This may involve measurement of the resistivity of the alumina or purchase of a higher grade of material that has a certified resistivity rating.

c. The effects of different electrode materials on other liquid metal systems should be tested. This should be carried out with a view to recommending electrode/sample pairs that have minimal reaction.

Acknowledgements

This work was carried out as part of the Materials Measurement Programme of the Department of Trade and Industry.

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Appendix A

An uncontrolled copy of the procedure for Measurement of Electrical Resistivity of Metals by the Four Probe Method, procedure number QPDMM/B/141.

Title: UNCONTROLLED
The Measurement of Electrical Resistivity of Metals by the Four Probe Method

CONTENTS

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4 STAFF REQUIREMENTS

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11 FURNACE SETUP

12 DATA STORAGE

13 ERROR ASSESSMENT

1 INTRODUCTION

1.1 This document describes the procedures used for the measurement of electrical resistivity of liquids using the four probe technique in the High Temperature Physical Properties Group in the Centre for Materials Measurement Technology.

1.2 The aim of the document is to provide the reader with the information required to make measurements with the Four Probe Method for measuring electrical resistivity.

2 DEFINITION OF ELECTRICAL RESISTIVITY

2.1 Resistivity (ρ) is the tendency to oppose the flow of an electrical current and is described by the following equation

$$\rho = \frac{RA}{l} \quad \mu\Omega cm \qquad (1)$$

where **R** is the resistance of the sample in Ω

A is the cross sectional area of the sample in cm^2

l is the distance between the potential measuring electrodes in cm.

For liquids a cell is used to contain the sample. It is more convenient to use a calibrant (Hg) of known resistivity to define the geometry of the sample rather than measure the area and length directly. Therefore the equation used when measuring electrical resistivity is as follows

$$\rho_S = R_S \frac{\rho_{Cal}}{R_{Cal}} \quad \mu\Omega cm \qquad (2)$$

where subscripts **S** and **Cal** denote sample and calibration respectively.

3 GENERAL DESCRIPTION OF THE TECHNIQUE

3.1 Overview of making a single Electrical Resistivity Measurement of a Liquid

3.1.1 The probe needs to be prepared. It may need to be cleaned depending on its previous use. It needs to be air dried from ethanol.

3.1.2 The probe needs to be calibrated using triple distilled mercury at 20°C +/-0.3°C, prior to any resistivity measurement (mercury is a well characterised material with an electrical resistivity of 95.6 $\mu\Omega$ cm^{-1}).

3.1.3 The material to be measured needs to be held in a suitable container within a thermostat bath, oven or furnace with top access for the probe. Thermal stability is important.

3.1.4 The probe needs to be immersed in the test liquid to a depth to cover the electrode wires by 3mm to 5mm.

3.1.5 The probe needs to be connected to the measurement system (i.e. the two fluke multimeters and power supply) using the standard cable and plug/socket connectors. This automatically connects the current and the potential measurement leads.

3.1.6 The thermocouple circuit needs to be connected via the Type R compensating connectors and compensating leads to the Thermocouple Amplifier.

3.1.7 The electronic measuring equipment needs to be switched on and initialised.

3.1.8 The standard resistor must be set to the required value.

3.1.9 Obtain satisfactory current and potential measurement and determine the resistance of the triple distilled Hg or the resistivity of the sample.

3.1.10 Simultaneously record temperature of the test liquid.

3.1.11 Repeat steps 9 to 10 to obtain satisfactory average value for the resistance of the triple distilled Hg or resistivity of the sample and temperature (conveniently six measurements).

3.1.12 If no more measurements are to be made, switch off output of power supply and fluke multimeters. Disconnect probe. Remove probe from test liquid and clean or change temperature of test liquid and repeat steps 7 to 11 as appropriate.

4 STAFF REQUIREMENTS

4.1 The apparatus is designed to operated as simply as possible. the minimum staff requirement is:

4.1.1 Research scientist, suitably trained assistant research scientist or student.

4.2 Qualified Staff

Dr B J Monaghan

5 EQUIPMENT LIST

5.1 The equipment is situated in room 28, building 13

5.2 The equipment consists of :

HP Vectra computer, printer	(data processor, IEEE488 bus controller)
Fluke 8840A Multimeter	(voltage measurement)
Fluke 8840A Multimeter	(current measurement)
Fluke 8840A Multimeter	(thermocouple measurement)
Thurlby Power Supply	(D.C. power source)
NPL Thermocouple Amplifier	(probe thermocouple temperature)
N.P.L. standard resistor	
Thermostat bath	
Furnace	

6 IDENTIFICATION OF TEST MATERIAL

6.1 Materials will be marked, stored and recorded according to the procedures listed in

procedure document QPDMM/B/127

7 PREPARATION OF SAMPLES

7.1 Sample should be liquid preferably homogeneous in nature at desired measurement temperature.

7.2 25 to 60 ml of sample should be poured /placed in a suitable receptacle and allowed to equilibrate with respect to measurement temperature, as in section 3.1.3.

7.3 A suitable receptacle is a closed bottomed cylinder of minimum internal diameter 25mm and height greater than 60mm. The choice of cylinder material will be dependent on nature of sample and temperature range of required thermal resistivity measurement.

8 AN OVERVIEW OF THE ELCOND5 SOFTWARE/HARDWARE

8.1 In the following section, bold type is used to indicate screen prompts and italics for operator keyed replies.

8.1.1 "*ENTER*" implies that a reply needs to be terminated by pressing the Enter/return key.

8.1.2 Function key responses are shown *[ ]*. Thus *[F3]* means press the function key F3. *[ ]* + *[ ]* means press these keys simultaneously. *[ ], [ ]* means press these keys in sequence.

8.1.3 ELCOND5 controls all operations via HPIB displaying all necessary prompts and error detection.

8.1.4 This program is compatible with disk stored data from previous versions of ELCOND.

8.1.5 ELCOND5 produces a measurement of resistivity of a sample.

8.2 Setting up and initializing ELCOND5

8.2.1 To run ELCOND5

8.2.1.1 At **PAM Main Menu** select **BASIC LANG PRO** by scrolling down the menu and pressing *ENTER*.

8.2.1.2 To load ELCOND5, press *[F5]*, type *ELCOND5* within the inverted commas, press *ENTER* then *[F3]*.

8.2.2 Follow screen prompts for **SETTING UP PROCEDURES**.

8.2.2.1 Any failure will require a re-run (Exit to **PAM**: *[Ctrl]* + *[F10]*, select **BASIC LANG PRO** by scrolling down the menu and pressing *ENTER* then *[F3]*)

8.2.2.2 A **Date** is shown on screen, if the **Date** is correct press *Y* (yes) and continue onto 8.2.2.3. If **date** is incorrect press *N* (no) and follow screen prompts to enter the correct **date.**

8.2.2.2.1 Delete **day** shown on screen using the *backspace key* and key in the day e.g. *05* then *ENTER* for a date 5-4-98.

8.2.2.2.2 *Apr* for the 4rth month then *ENTER*, then

8.2.2.2.3 *1998* and *ENTER* for the year 98

8.2.2.2.4 If new **date** shown is correct then press *Y* and go to 8.2.2.3. If incorrect press *N* and return to 8.2.2.2.1.

8.2.2.3 A **time** is shown on screen, if the **time** is correct press *Y* (yes) and continue onto 8.2.2.4. If the **time** is incorrect press *N* (no) and follow screen prompts to enter the correct **time.**

8.2.2.3.1Input the no of hours e.g. for 2.30pm, input *14* then *ENTER.*

8.2.2.3.2 Input the number of minutes, in this case *30* then *ENTER.*

8.2.2.3.3 Input the number of seconds, in this case *0* then *ENTER.*

8.2.2.3.4 If new **time** shown is correct then press *Y* and go to 8.2.2.4. If incorrect press *N* and return to 8.2.2.3.1

8.2.2.4 Input the **First run number** and press *ENTER*- thereafter program increments run number following successful **Write to disc**.

8.2.2.5 Input the **Standard resistor** value and press *ENTER*- invariably around 0.5 ohms. Dependent on standard resistor setting and calibration.

8.2.2.6 Input the **Cell resistance in mercury** and press *ENTER*- if a cell calibration run is being carried out enter *-1* and press *ENTER*.

8.2.2.7 Input the **Thermocouple amplifier gain** (typically *100*) and press *ENTER*. See front panel of amplifier in use.

8.2.2.8 Program now moves into the **control menu**.

8.2.3 Description of the **control menu** options.

8.2.3.1 To select the different options available on the **control menu** shown below, input the number on the left hand side of the menu adjacent to the required option i.e. to select **Process data** input *3*.

(1) Set variables

(2) Run experiment

(3) Process data

(4) Check temperature

(5) Spot reading

(6) Printout

(7) Write data to disc

(8) Surge electrodes

(9) Change parameter settings

An explanation of 1 to 9 is given below.

8.2.3.2 **(1) Set variables** branches to **EXPERIMENTAL PARAMETERS** setup.

8.2.3.2.1 Input name of the **Material** e.g. *Three letter code* and press *ENTER*.

8.2.3.2.1.1 The operator is now offered two choices to **Measure resistance against**:

(1) time

(2) temperature

To select **time** or **temperature** input *1* or *2* and go to 8.2.3.2.1.2 or 8.2.3.2.1.8 respectively

8.2.3.2.1.2 Input time **Interval between readings** in seconds and press *ENTER*, typically 5 seconds for measurements made at a static temperature.

8.2.3.2.1.3 Input **Settling time delay** in seconds or fractions thereof and press *ENTER*, typically 0.5 seconds.

8.2.3.2.1.4 Input **Current limit** in amps and press *ENTER*. Typically 1 amp but can be anything from 0.01 to 10.00 amps.

8.2.3.2.1.5 Input **Starting voltage** in volts and press *ENTER*. Typically 0.5 V but can be anything from 0.00 to 10.00 volts.

8.2.3.2.1.6 Input **Incremental voltage** in volts and press *ENTER*. Typically 0 volts. The increment can be anything from 0.00 to 10.00. If the incremental voltage is 0 then 8.2.3.2.1.7, if > 0 then the program will prompt the user to input a **maximum voltage.** Input a **maximum voltage** and press *ENTER*, the program will then return to the **control menu**.

8.2.3.2.1.7 Input **Number of repeat measurements** and press *ENTER*. Typically 6 for measurements made at a static temperature or 1 for measurements made during heating or cooling. The number of repeat measurement must be ≤ 100. The program will then return to **control menu**.

8.2.3.2.1.8 Input a **starting temperature** in °C and press *ENTER*.

8.2.3.2.1.9 Input the **temperature interval** you wish to increment your measurements by and press *ENTER*. This should be prefixed by + on a heating cycle and - on a cooling cycle, e.g. to take readings every 5°C on a cooling cycle input *-5* and press *ENTER*.

8.2.3.2.1.10 Input the **finishing temperature**, i.e the temperature you wish to stop taking measurements at and press *ENTER*. Then follow set **Voltage** (8.2.3.2.1.5), **Current limit** (8.2.3.2.1.4) and **Settling time delay** (8.2.3.2.1.3) .

8.2.3.3 **(2) Run experiment**, carries out the experiment according to input parameters in **Set variables**. Once measurements are completed press *any key* to return to the **control menu**.

8.2.3.4 **(3) Process data**, displays a table with of all parameters measured, (time, temperature, current and voltage) as well as properties calculated (resistance and resistivity).To return to the **control menu** press *any key*.

8.2.3.5 **(4) Check temperature**

8.2.3.5.1 Select *4* and press *space-bar* Thermocouple DMM is interrogated. Temperature is calculated for Type R thermocouples from polynomial expressions.

8.2.3.5.2 Out of range values give rise to a warning message.

8.2.3.5.3 Press *Q* to exit **Check temperature** and return to the **control menu**.

8.2.3.5.4 To change the **Thermocouple amplifier gain** within **select temperature** press *G*.

8.2.3.6 **(5) Spot Readings** !!! do not use this setting as it will lock up machine!!!

8.2.3.7 **(6) Printout** - causes hardcopy of current file to be generated on printer. Follow instructions on screen. Data is output as a table with of all parameters measured, (time, temperature, current and voltage) as well as properties calculated (resistance and resistivity). Once the **Printout** is complete the program returns to the **control menu**.

8.2.3.8 **(7) Write data to disc** - Follow instructions on screen. Disc needs to have been

formatted previously.

8.2.3.8.1 Data is written to floppy disc in Drive A under a file number which is the **Run number**. **Run number** is then incremented by one.

8.2.3.9 **(8) Surge electrodes**, is used to remove oxide from the electrodes. To **enter surge parameters** follow screen prompts

8.2.3.9.1 Input **Voltage** in volts and press *ENTER*. Typically 10 volts.

8.2.3.9.2 Input **Duration** of applied voltage in seconds and press *ENTER*. Typically 1 second.

8.2.3.9.3 Input **Current limit** in amps and press *ENTER*. Typically 10 amps.

8.2.3.9.4 A screen with **Experimental options**

(1) Normal polarity (polarity currently in use)

(2) Reverse polarity (opposite of polarity currently in use)

In general select *2* when using the surge option

8.2.3.9.5 On selecting a polarity the following options will appear

(1) Return to main menu after surge

(2) Proceed direct to measurement

In general select *1* when using the surge option

8.2.3.9.6 On selecting *1* or *2* from above you will be asked

Ready: are you sure?

if yes press *Y* and go to 8.2.3.9.7

if no press *N* to return to the control menu

8.2.3.9.7 **Check standard resistor is set to zero**

If not change the standard resistor to zero.

If so press *space bar* to initiate the surge

8.2.4 **(9) Change parameter settings**. This option enables changing of the setting up conditions e.g. run no. etc from within the program. Go to 8.2.2.4

8.3 Hardware readout displays.

8.3.1 Voltage DMM displays potential drop through the sample.

8.3.2 Current DMM displays current through the cell.

8.3.3 Thermocouple DMM indicates thermocouple emf * amplifier gain.

8.3.4 Power source displays voltage

8.4 Errors

8.4.1 Failures during the initialisation procedure are not recoverable. They are usually due to an IEEE488 bus fault, frequently failure to switch on an item of equipment. Correct

the cause and re-run the program *[F3]*.

8.4.2 Once initialised, operator errors are (mostly) recoverable. A warning message is displayed together with instructions for correction. (*[F2]* clears the error and returns the program to **the control menu**.) The current data set, if complete, is not lost.

8.4.3 IEEE488 bus faults cause the system to "hang". It may be possible to rectify the fault but treat any current data with suspicion. In general it is best to exit to **PAM** (*[Ctrl]* + *[F10]*), enter **BASIC LANG PRO** and re-run (*[F3]*).

9 MAKING A MEASUREMENT

To make a resistivity measurement on a liquid metal using the NPL four probe method, the probe must be calibrated first using triple distilled Hg. The calibrated probe will then be used to measure the liquid metal sample.

The measurement example in the section is for measuring resistance against time not against temperature. For measuring resistance against temperature see section 8.2.3.2.1.8 to 8.2.3.2.1.10.

As in section 8, **Bold** and *italics* are used in this section to represent screen prompt and operator inputs respectively.

9.1 Switch on:

Unit	Function

9.8 Input the **Thermocouple gain** (typically 100) and press *ENTER*.

9.9 At the **control menu** select *1* to **set variables** (experimental).

9.9.1 Select *1* to make readings against **time**.

9.9.2 Input **Material** name and identification, ie three letter metal store code, and press *ENTER*

9.9.3 Input **Time interval between readings** in seconds and press *ENTER*. Typically 5 seconds for static temperature measurements.

9.9.4 Input **Settling time** delay in seconds and press *ENTER*. Typically 0.5 seconds.

9.9.5 Input **Current limit** in amps and press *ENTER*. Typically 1 amps.

9.9.6 Input **Starting voltage** in volts and press *ENTER*. Typically 0.5 volts.

9.9.7 Input **Incremental voltage** in volts and press *ENTER*. Typically 0.

9.9.8 Input **Number of repeat measurements** and press *ENTER*. Typically 6.

9.10 The program then returns to the **control menu**. select *2* to **Run experiment** and make a resistivity measurement.

9.8 Input the **Thermocouple gain** (typically 100) and press *ENTER*.

9.9 At the **control menu** select *1* to **set variables** (experimental).

9.9.1 Select **1** to make readings against **time**.

9.9.2 Input **Material** name and identification, ie three letter metal store code, and press *ENTER*

9.9.3 Input **Time interval between readings** in seconds and press *ENTER*. Typically 5 seconds for static temperature measurements.

9.9.4 Input **Settling time** delay in seconds and press *ENTER*. Typically 0.5 seconds.

9.9.5 Input **Current limit** in amps and press *ENTER*. Typically 1 amps.

9.9.6 Input **Starting voltage** in volts and press *ENTER*. Typically 0.5 volts.

9.9.7 Input **Incremental voltage** in volts and press *ENTER*. Typically 0.

9.9.8 Input **Number of repeat measurements** and press *ENTER*. Typically 6.

9.10 The program then returns to the **control menu**. select *2* to **Run experiment** and make a resistivity measurement.

9.10.1 Press *any key* to return to the **control menu** at end of the measurement.

9.11 Select *3* to (view) **process data.**

9.11.1 Press *any key* to return to the **control menu** after viewing.

9.12 Select *7* to **save data to disk**.

9.12.1 Press *any key* to **save data**.

9.13 To reuse the same measurement setup select *2* to **Run experiment** and follow steps 9.8 to 9.12. To reset measurement setup repeat steps 9.7 to 9.10. To end measurements *[Ctrl]+[F10], turn off equipment* listed in 9.1.

10 CALIBRATION OF THE STANDARD RESISTOR

The standard resistor used in the electrical resistivity measurement technique must be calibrated at least once every year.

10.1 Equipment needed

10.1.1 A calibrated multimeter with sensitivity to 0.1 mΩ. It is recommended that a Fluke 8842A is used.

10.1.2 One set of 4-probe leads with plug and crocodile clips.

10.2 Calibration of the standard resistor

10.2.1 Turn on multimeter

10.2.2 Remove light grey lid from the standard resistor

10.2.3 Connect crocodile clips to the resistor points

10.2.3.1 Connect the potential leads (thin leads) on the resistor points

10.2.3.2 Connect the current leads (thick leads) on the bare wire

10.2.4 Plug the leads into the four probe sockets of the multimeter

10.2.4.1 Plug the potential leads (thin leads) into the sense sockets

10.2.4.2 Plug the current leads (thick leads) into the main input sockets

10.2.5 Set the multimeter to 4 probe (4 wire in the case of Fluke 8842A) setting with sensitivity of at least 0.0000Ω

10.2.6 Let the setup stabilise for at least 15 minutes

10.2.7 Take 5 resistance readings for each setting on the standard resistor, taking care to ensure that the setup has stabilised between each resistor setting

10.2.8 Disconnect the crocodile clips from the standard resistor, replace cover

11 FURNACE SETUP

Schematics of the furnace setup, resistivity probe and seal setup are given in Figures 1, 2 and 3 respectively.

11.1 Prior to setting up the furnace ensure that the o-ring seals on the silica tubing, shown as ● in Figure 1 are in good condition.

11.2 The resistivity probe (shown in Figure 2) and electrodes are fixed to the stainless steel head via the o-ring seals as shown in Figure 3. **Care must be taken not to over tighten these seals when attaching the probe to the stainless steel head. Also the operator must ensure that when placing the electrodes in the silica probe that the electrodes do not enter the lower U-tube.**

11.3 To ensure there is no electrical leakage to the stainless steel head the electrodes are isolated from it using heat shrink insulation, as shown in Figure 3. **Care must be taken to ensure that the electrode does not come in contact with the stainless steel head, therefore leave around 10 mm excess heat shrink on either side of the electrode stainless steel head junction.**

11.4 The resistivity probe should be setup such that, when it is placed in the furnace, the bottom of the probe is at least 330 mm from the top of the furnace chamber. This dimension is best shown in Figure 3.

11.5 The probe electrodes are connected to the measuring system via a set of colour coordinated leads such that each of the upper U-tubes shown in Figure 2 has one potential tap (thin wire+electrode) and one current lead (thick wire+electrode). The wire colouring for each U-tube electrode set (thin wire+electrode and thick wire+electrode) should be the same.

11.6 Before placing the probe/stainless steel head in the furnace the crucible and sample should be at the lowest point in the furnace.

11.7 Once the crucible and sample has be placed in the furnace at the lowest point, and the probe/stainless steel head sealed on the copper end, gas should be bled through the furnace at a slow bubble rate for at least two hours.

11.8 After two hours the furnace can then be run up to temperature using the Eurtherm controllers (see the Eurtherm controller manual located on the shelf above and to left of the furnace). The starting temperature must be above the liquidus temperature of the materials being measured.

11.9 Once the desired temperature has been reached the probe is inserted by raising the crucible and sample until a voltage is registered on the current multimeter to achieve this:

11.9.1 Set both the current and voltage multimeters to local control (not PC) and automatic reading (see multimeter manuals located on the shelf above and to left of the furnace).

11.9.2 Set a the power supply on local control and set a voltage on the power supply of around 0.5 Volts (see power supply manual located on the shelf above and to left of the furnace). Under such conditions a current will flow through the probe as soon as the electrodes contact the liquid metal.

11.9.3 Set the speed dial on the drive shaft (located below and to the right of the furnace) to 0.5.

11.9.4 Push and hold the toggle switch (located on the top right hand side of the furnace frame) up to raise the crucible and sample.

11.9.5 While raising the crucible and sample observe the current multimeter. As soon as it registers a voltage i.e. the electrodes make contact with the liquid metal, release the toggle switch. Note the position of the height indicator (located on the front right leg of the furnace support)

11.9.6 After contact is made reset the dial speed to 0.05 and raise the crucible and sample a further 5 mm.

11.10 The temperature of the system (probe plus liquid metal) must be allowed to stabilise for at least fifteen minutes.

11.11 The system is now ready to make resistivity measurements.

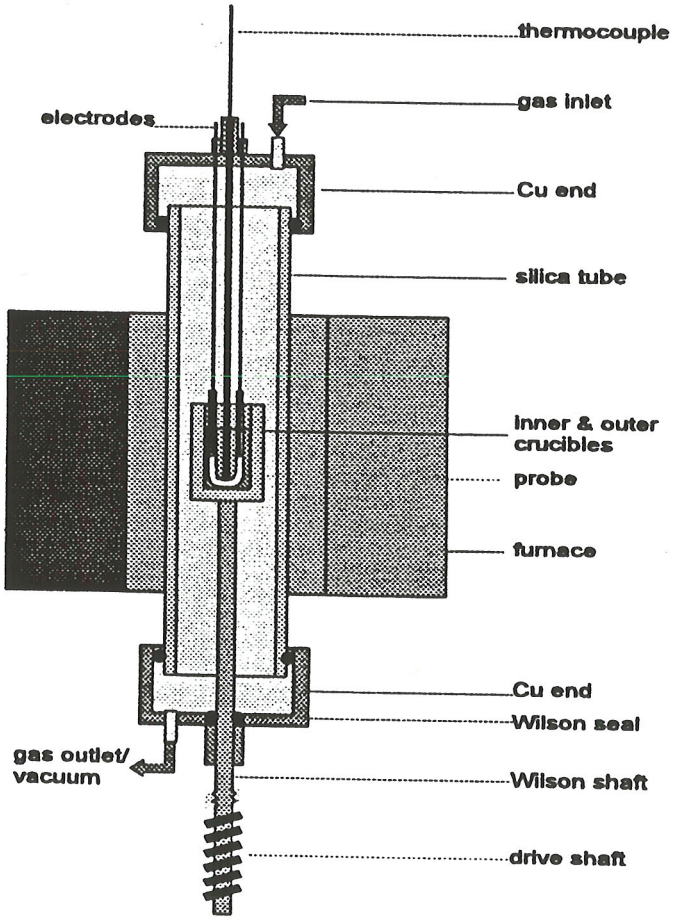


Figure 1 Furnace Setup

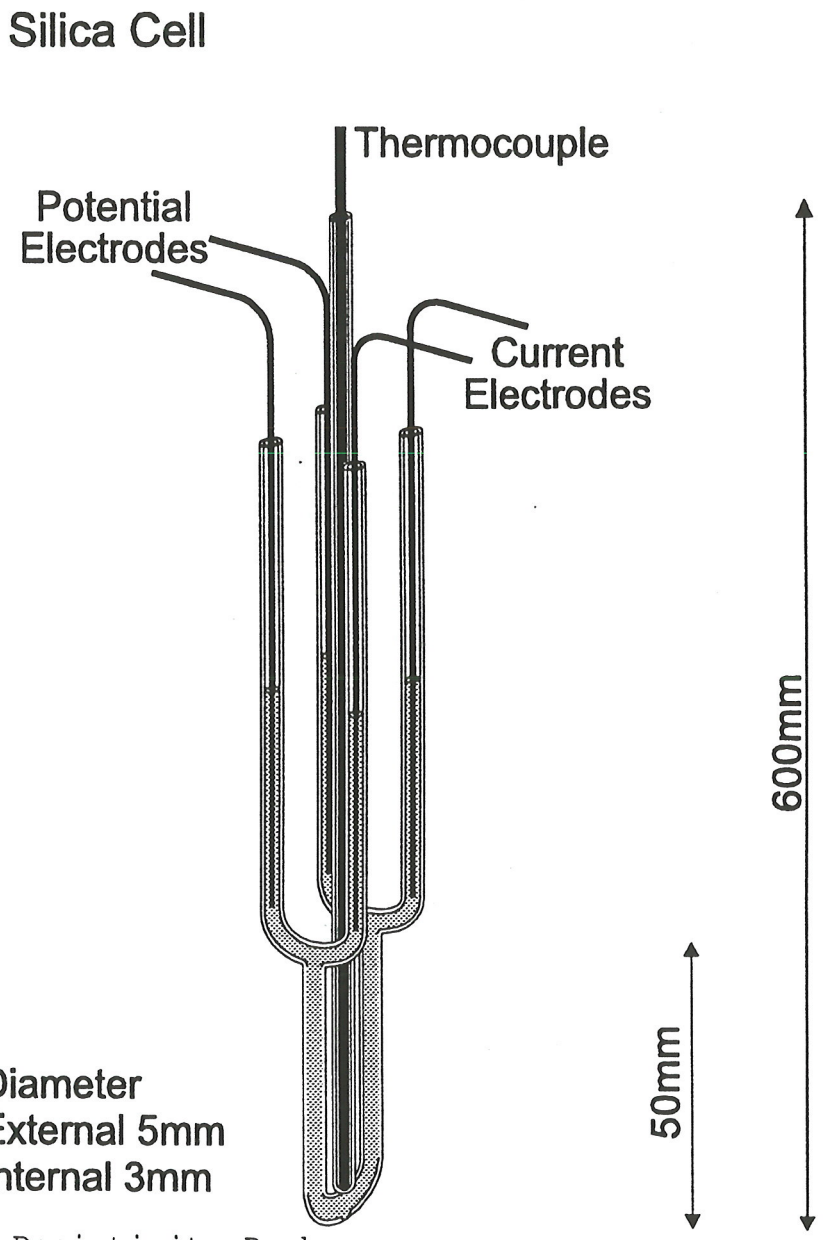


Figure 2 Resistivity Probe

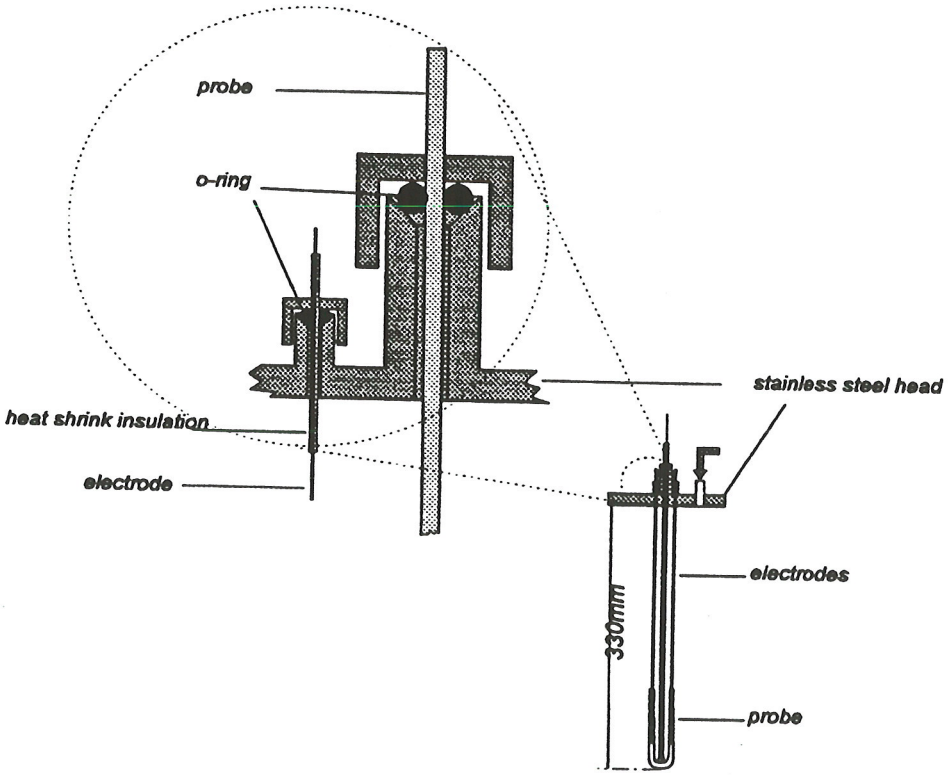


Figure 3 Detailed seal and probe setup

12 DATA STORAGE

12.1 Primary Data Storage.

12.1.1 3½" high density disk. Disk is kept next to measurement computer until full then stored in R40 B13 marked ER(NUMBER-NUMBER).

12.1.2 Full disks are also copied and compressed using Winzip onto Brian Monaghan's PC, Room 40, B13, path C:\ecbackup\er.zip.

12.1.3 Brian Monaghan's PC is backup onto tape cartridge, regularly and stored at his personal residence.

12.2 Secondary Data (Calculations and graphs derived from primary data)

12.2.1 Stored on B Monaghan's PC room 40 B13, path C:\mydocuments\workxl\econd\.

12.2.2 File names using said data will be noted in the Electrical Resistivity Notebook, stored in R40 or 28, B13.

13 ERROR ASSESSMENT

13.1 Errors in the four probe resistivity technique are assessed below.

Standard values used in calculation

Hg standard	95.6	μΩcm
Vcalibration	0.0075	V
Vcalibration(current)	0.311	V
Standard Resistor	0.5026	Ω
Cell constant Rcal	0.01212	Ω
Vsample	0.003	V
Vsample(current)	0.2	V
Resistance of sample	0.0075	Ω
Resistivity of sample original data	59.5	μΩcm

Source of Uncertainty	**value (+/-)**	**units**
recommended value of Hg	0.956	μΩcm
temperature of standard	0.3	°C
resolution in Voltage measurement of calibrant	0.0159	μΩcm
resolution in Voltage (current) measurement of calibrant	0.0004	μΩcm
standard deviation of Cell constant	0.0033	μΩcm
temperature of sample	3	°C
resolution in Voltage measurement of sample	0.0396	μΩcm
resolution in Voltage (current) measurement of calibrant	0.0006	μΩcm
electode reativity (low)	1	%
electode reativity (high)	2	%

uncertainty calculated using NIS 3003

standard deviation resistivity of sample	0.2	μΩcm
uncorrected mean value of the measurand (NIS 3003 equ. 5)	0.1	μΩcm
combined standard uncertainty for low electrode reactivity (NIS 3003 equ. 9)	0.8	μΩcm
combined standard uncertainty for high electrode reactivity (NIS 3003 equ. 9)	1.3	μΩcm

A coverage factor of 2 gives a 95% confidence limit

low electrode reactivity	1.7	μΩcm
high electrode reactivity	2.6	μΩcm

Evaluation of errors are found in the EXCEL Spreadsheet file C:\mydocuments\workxl\econd\er_erro1.xls on B Monaghan's PC R40 B13.

Appendix B

The heat capacity data, density and thermal diffusivity data used in the three layer model to calculate the thermal diffusivity of the slag.

Temperature, °C	Heat Capacity, $Jg^{-1}K^{-1}$
20	0.1420
100	0.1460
200	0.1490
300	0.1530
400	0.1570
500	0.1600
600	0.1630
700	0.1660
800	0.1690
900	0.1730
1000	0.1760
1100	0.1790
1200	0.1820
1300	0.1850
1400	0.1880
1500	0.1900
1600	0.1940
1700	0.1970
I740	0.1980

Table B1. Heat capacity values of the platinum cell.

Temperature, °C	Density, gcm^{-3}
20	20.000
100	19.956
200	19.900
300	19.842
400	19.783
500	19.722
600	19.660
700	19.597
800	19.532
900	19.464
1000	19.395
1100	19.320
1200	19.252
1300	19.177
1400	19.099
1500	19.017
1600	18.933
1700	18.850
1800	18.767

Table B2. Density values of the platinum cell.

Temperature, °C	Thermal Diffusivity, cm^2s
28	0.1371
195	0.1630
392	0.1840
588	0.1973
794	0.2075
996	0.2175
1190	0.2221
1405	0.2290
1600	0.2338
1700	0.2358
1800	0.2373

Table B3. Thermal diffusivity values of the platinum cell.

Temperature, °C	Heat Capacity, $Jg^{-1}K^{-1}$
1000	1.4443
1100	1.4443
1200	1.4443
1300	1.4443
1356	1.4443
1357	1.4443
1400	1.4443
1500	1.4443
1600	1.4443
1700	1.4443

Table B4. Heat capacity values of ASK

Temperature, °C	Density, gcm^{-3}
1000	2.6386
1100	2.6111
1200	2.5842
1300	2.5578
1356	2.5433
1357	2.543
1400	2.532
1500	2.5067
1600	2.4819
1700	2.4575

Table B5. Density values of ASK

Temperature, °C	Density, gcm^{-3}	Heat Capacity, $Jg^{-1}K^{-1}$
All temperatures	2.7	1.35

Table B6. Density and specific heat values of ASE