

REPORT

Measuring the Density of Liquid Metals Using the Levitated Drop Method

A McCormick

December 1998

Measuring the Density of Liquid Metals Using the Levitated Drop Method

A McCormick
Centre for Materials Measurement and Technology
National Physical Laboratory
Teddington
Middlesex, UK, TW11 0LW

SUMMARY

This report details the steps taken to improve the levitated drop method for measuring the densities of liquid metals. These improvements include:

- (a) new coil design to handle high melting metals like titanium
- (b) the introduction of digital cameras to capture the image of the drop which led to (i) more efficient and faster processing of the image analysis and (ii) the extension of the method to low-melting metals since these cameras are much more sensitive to light from low emitting sources.

An uncertainty budget has been carried out and this has identified the error associated with edge detection to be the major source of uncertainty in the density measurement. Values have been obtained for several molten metals, the relative differences between the measured and recommended values are Cu (+0.6%), Fe (+1%) Sn (-2%) and Ti- 6Al-4V (-1%).

© Crown copyright 1998
Reproduced by permission of the Controller, HMSO

ISSN 1361-4061

National Physical Laboratory
Teddington, Middlesex TW11 0LW, UK

Extracts from this report may be reproduced provided the source is acknowledged.

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

CONTENTS

1	INTRODUCTION
2	DEVELOPMENT OF THE LEVITATED DROP METHOD
3	ANALYSIS OF THE PHOTOGRAPHED IMAGES
3.1	PRINCIPLE
3.2	METHOD
4	USING DIGITAL CAMERAS
5	DEVELOPMENT OF TECHNIQUE FOR HIGH MELTING POINT ALLOYS
6	LOW MELTING POINT ALLOYS
7	TEMPERATURE MEASUREMENTS
8	CONCLUSIONS AND FUTURE WORK
9	UNCERTAINTY BUDGET
9.1	ERRORS IN TEMPERATURE MEASUREMENT
9.2	ERRORS IN EDGE DETECTION
9.3	ERRORS DUE TO MASS LOSS
10	TABULATED DATA
11	REFERENCES

1 INTRODUCTION

The density ρ and temperature dependence $\frac{d\rho}{dT}$ of commercial alloys are needed to compute the magnitude of the buoyancy forces operating in the molten metals or the 'mushy zone' in process, and solidification models.

There are several methods available for the determination of the density of melts such as sessile drop, maximum bubble pressure, arcmedian and hydrostatic probe. The levitated drop method [1,2] has the advantage over conventional methods that

- (1) it can be applied over a large temperature range and thus can provide accurate values of $\frac{d\rho}{dT}$
- (2) it eliminates the possibility of contamination of the metal by melt /container reactions (which are prevalent at high temperature and can lead to errors in conventional techniques).

The principle disadvantages of the measurement are the uncertainty of the temperature measurement of the sample and the loss of mass due to evaporation.

The technique is to photograph an axi-symmetric droplet of known mass, and then from the pictures determine the volume of the drop. In the previous program (DTI Programme for Materials Processability PMP1) the technique was developed to measure the density of commercial alloys to within an experimental uncertainty of $\pm 2\%$, but technical problems limited the temperature range to 1200 °C-1700 °C. Whilst this range is sufficient for most of the Fe, Ni and Co based alloys, many industrially significant alloy systems such as Cu, Al and Ti lay outside this range. The aim of this work was to extend the temperature capabilities of the apparatus: to both higher, and lower temperatures to 2000 °C to measure a highly reactive Ti alloy; and to discover the lower temperature limit of the system.

2

DEVELOPMENT OF THE LEVITATED DROP METHOD

Levitation melting has been used for several years at NPL to measure the surface tension of molten metals and alloys [3]. The experience and expertise acquired has proven very useful in the development of the method for the determination densities of molten metals and alloys.

The basic apparatus is shown in Figure 1, and contains the following features:

- (i) the use of an optically flat, square-section silica tube to obtain an undistorted image
- (ii) a special levitation coil capable of lifting the sample out of the lower coils to provide a clear view of the drop
- (iii) the use of three synchronously triggered cameras, sighted in mutually orthogonal directions
- (iv) a reference ball to scale images at room temperature

- (v) a turntable to allow reference ball and samples to be loaded without dismantling the equipment
- (vi) pyrometer for measuring temperatures.

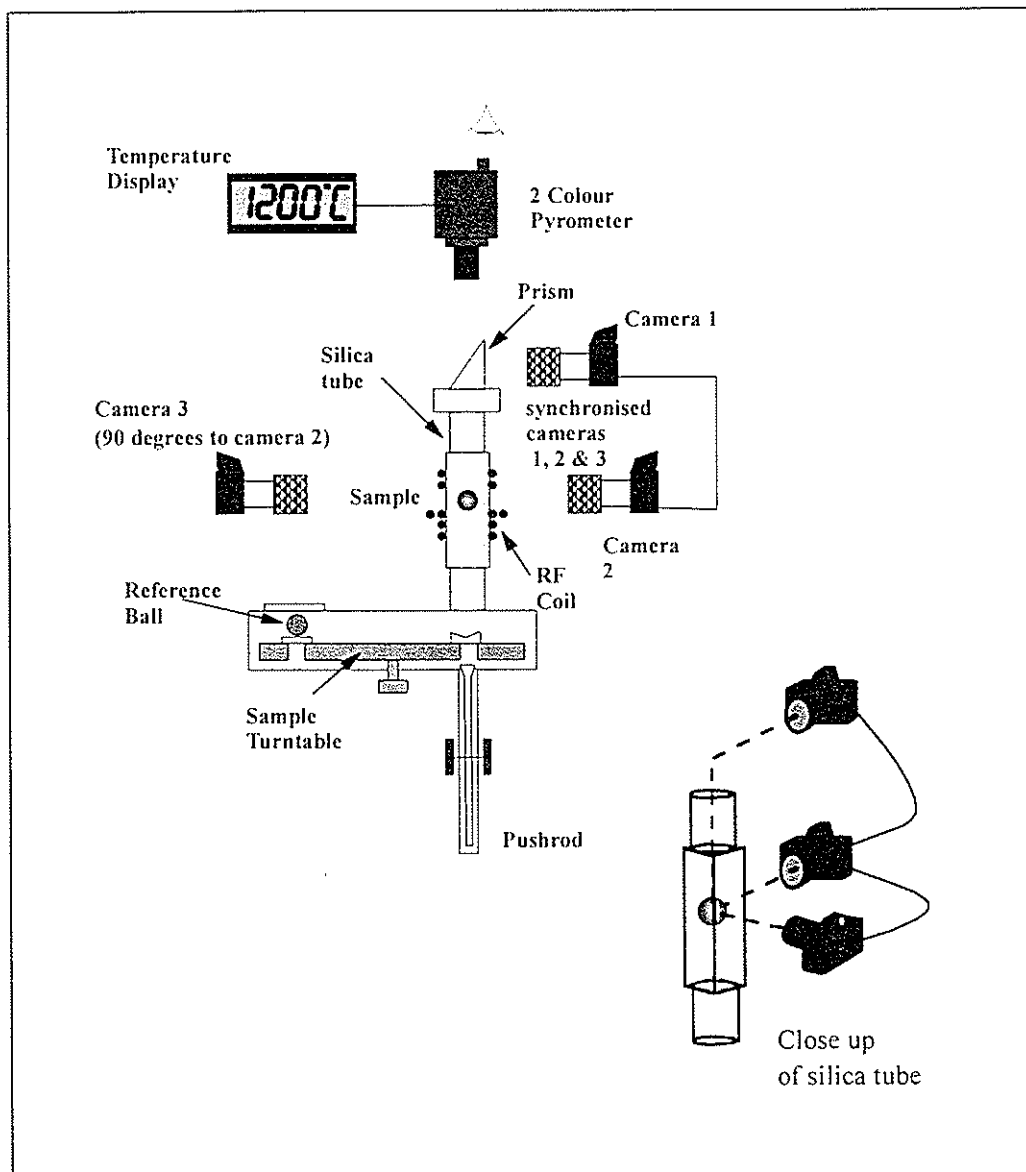


Figure 1 The levitation apparatus for density measurement.

The apparatus is run in a similar way to that used in surface tension measurements[3]: A sample is levitated and inductively heated in the magnetic field of an RF coil, operating at 300 kHz.. An atmosphere of argon and a gas of higher thermal conductivity, such as He (inert atmosphere) or H₂ (reducing atmosphere) is passed through the apparatus. The temperature of the drop is controlled by varying the ratio of these gases. By increasing (or decreasing) the He or H₂ ratio more (or less) heat is extracted from the sample and so its temperature can be controlled. The temperature of the molten sample (T_{meas}) is measured using a commercial 1 or 2 colour pyrometer focused on the drop.

To determine the volume of the sample from a single side elevation requires the drop to be axis-symmetric, and for radii to be measured along that axis. However, because the shape of the levitated droplet is constantly changing (oscillating - the basis of surface tension measurements by this technique) it is necessary to view the drop from both the top (the direction of symmetry), and the side (along the axis of symmetry). Two 35mm cameras are employed (Nikon 501), with a third to provide a check on the side view. Because the shape of the drop is constantly changing at a rate of 50Hz, the opening of the shutters has to be synchronised to within 3ms to ensure the same oscillation is captured by each camera. It was found that the response of the shutter to a signal varied for each camera. It was therefore necessary to construct a 'bucket brigade' type circuit to delay the signals to the fastest reacting cameras so that they matched the slowest. Testing the shutters with a photodiode and an oscilloscope found that a 3 millisecond response could be achieved. The control circuit included a feedback from the camera flash contacts which monitored when each camera fired during the measurements. Frames identified where the cameras failed to synchronise could therefore be excluded.

3 ANALYSIS OF THE PHOTOGRAPHED IMAGES

3.1 PRINCIPLE

The principle of the method is to identify a circular drop on the film taken from the camera which looks at the drop from the top (camera 1), and then use the corresponding image taken from the camera which looks from the side of the drop (camera 2 and 3), to determine the volume of the drop (Figure 2). The side view is assumed to be axis-symmetric if its corresponding top view is circular. The exact dimensions of the drop are determined by the comparison of the sample image with that derived for a sphere of known dimensions (6mm diameter) at ambient temperature when it is supported vertically on a pin. As each exposed reel of film includes a scaling image differences in magnification can be accounted for. Measurements are taken from each sample at a single temperature. This reduces the time required for each experiment and reduces the risk of vapour losses. The mass of the drop is determined before and after the levitation and the density can then be calculated from the volume and the mean mass, and thus, the losses due to vaporisation can be accounted for.

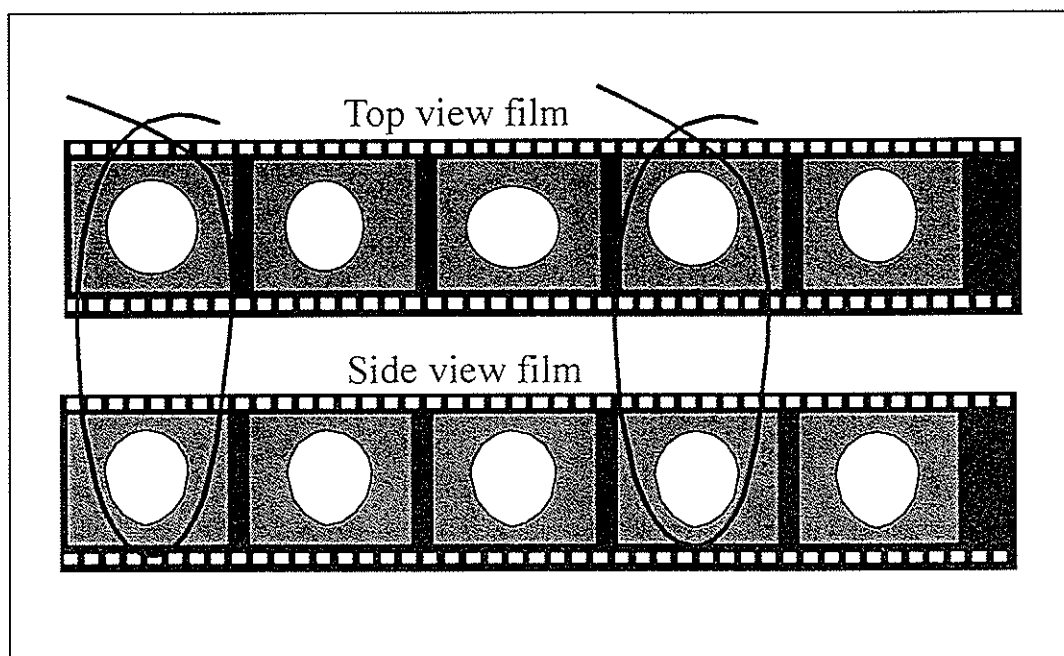


Figure 2 Selecting suitable images

3.2 METHOD

Negatives from the top view are assessed for circularity and acceptable frames are recorded. The calibration image and the selected side view images are scanned into a computer using a Polaroid Sprint Scan at a resolution of 2700dpi to provide digital images for processing. Two software packages and methods have been tried:

In the previous project a commercial programmable image analysis program (Semper 6 for windows) was used to determine the density of the drops. This used automatic edge detection to find the size of the drop. Whilst this was successful with clear images, poor quality pictures, for instance where the edge was partially obscured by vapour deposits on the tube, gave rise to errors. As Semper was designed for a Unix based system it also ran slowly on a PC based system.

A program was written at NPL to analysis the bitmap images (Levdrop v1.00 by Austin Day, NPL). This allows the operator to manually fit a set of nodes on the edge of the drop and the programme then calculates a curve to fit these points based on a distorted ellipse. The nodes can be adjusted so that an accurate fit is obtained. From the fitted shape the programme calculates the axis of symmetry and left and right radii along the axis at 1 pixel intervals. The uniformity of the fit can be checked by comparing these. From each radius a volume of revolution is calculated and summed to give a total volume. By first analysing the calibration ball image a scaling factor for subsequent images is given and is used, together with the mean mass of the sample and its temperature to give the density.

4 USING DIGITAL CAMERAS

The initial target of measuring the density of commercial alloys to within an experimental uncertainty of $\pm 2\%$ had been achieved with the use of 35 mm cameras. However the method was time consuming as it involved manually developing the film and scanning individual images into the computer. This would pass on a higher operating cost to potential customers.

With a digital camera the photograph could be taken and then directly down loaded to the computer taking out the need for developing and scanning. The time for each process could be reduced, thus lowering costs and making it more commercially viable .

It was important that the resolution of the images was not compromised too much and that the cameras could be synchronised. Also the camera would need to have the option of interchangeable lenses in order that the drop would fill the field of view so that the resolution could be maximised.

After some research it became apparent that most of the cameras were 'point and shoot', very few cameras had interchangeable lenses. The SLR type digital cameras which did have interchangeable lenses designed for professional use were expensive and not an option at the time. A mid-priced digital camera with a suitable specification (Kodak DC120 with resolution of 1290 X 960) was obtained and experiments made with a lens system to provide an image which would cover a large area of the camera c.c.d.. Mounting the camera on an optical bench with an objective lens close to the camera, and a 70 - 210 zoom lens some 350 mm away, with the camera fixed on macro focus, an acceptable image 800 pixels across could be obtained (compared with 850 pixels from the 35 mm camera set-up). Figure 3 shows the set-up used in order to magnify the drop sufficiently.

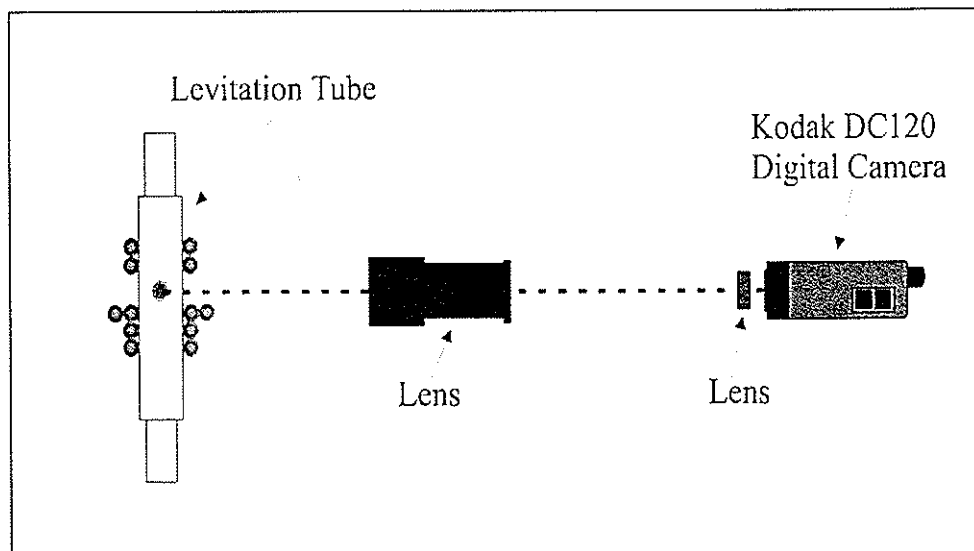


Figure 3 Set-up used to magnify the drop sufficiently.

The c.c.d. was found to be more sensitive to light than the 35 mm film in this set-up. As the aperture control of the camera could not be used a filter was placed between the two lenses to prevent overloading of the c.c.d. which resulted in flaring of the pixels and an apparently oversized image.

The next important step was how to synchronise a second camera. As the cameras could be individually triggered by supplied software a program was written as a Labview Virtual Instrument to control both cameras remotely by PC. By connecting camera cables in parallel and sending a signal via the serial port of the computer, both cameras could be fired simultaneously. The synchronisation was tested by taking a photo of a calibrated digital counter with a resolution of 1/1000 of a second. Images from 2 cameras showed agreement to better than 1ms, the requirement was to within 3ms.

To check the system Fe was measured again and the results were found to be within 1% of the previous results using standard SLR cameras, Figure 4.

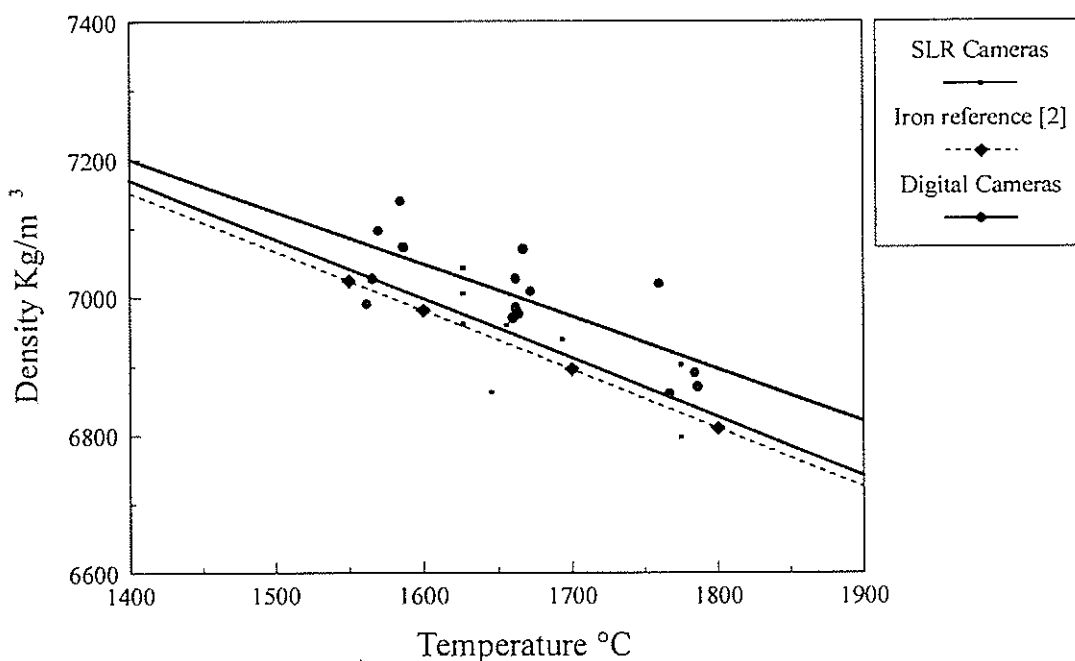


Figure 4 Comparison of standard SLR cameras to digital cameras for Fe.

5 DEVELOPMENT OF TECHNIQUE FOR HIGH MELTING POINT ALLOYS

Ti 6Al 4V was attempted in the last program but a coil could not be made that could both lift the droplet out of the windings and heat the sample. More power was required than the coil could accommodate to lift the titanium out of the coil so that the cameras had a clear view of the drop.

A new generator was installed which could run at lower frequencies and larger coil tubing diameters. This allowed for a more powerful, larger diameter coil, which could produce the required lift and heat input. The density results for Ti 6Al 4V are shown in Figure 5. It shows very close agreement with METALS [4] and has a spread of 1%. The temperature range was then limited by the range of the pyrometer, but was sufficient to provide a reasonable range to determine dp/dT for the alloy.

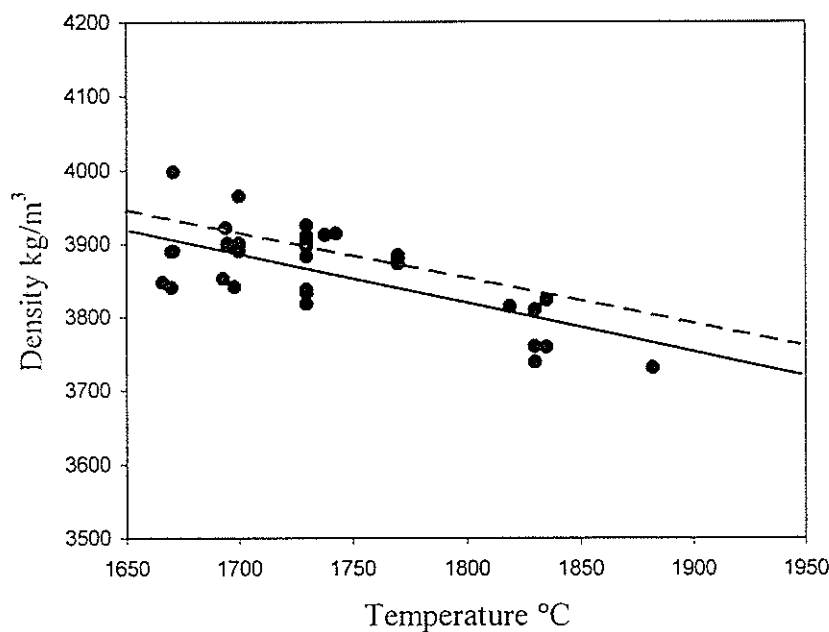


Figure 5 Density of Ti 6Al 4V

6 LOW MELTING POINT ALLOYS

The second part of the program was to extend the temperature range down to lower melting point alloys. It became apparent that the cameras were more sensitive to light than the standard SLR's, so droplets could be imaged at much lower temperatures than before. A Minolta Land 152A single colour pyrometer was used to measure the temperature of the samples. This had a quoted temperature range of 600 to 2000 °C, but it was found that the low emissivity of the samples combined with the small droplet size meant that the range was actually material (emissivity) dependent, and could not be relied upon below ca. 700 °C

Copper was measured down to 800°C (Figure 6) without any extra lighting techniques, and was shown to be within 0.6% of recommended data. Tin, having a higher emissivity, was measured down to an indicated 700°C (Figure 7), but it was not possible to obtain a temperature correction by the standard method (see section 7) because the melting point of Tin is below the temperature range of the pyrometer. The data was within 2.2% of METALS [4] and it would be expected to be less with a temperature correction.

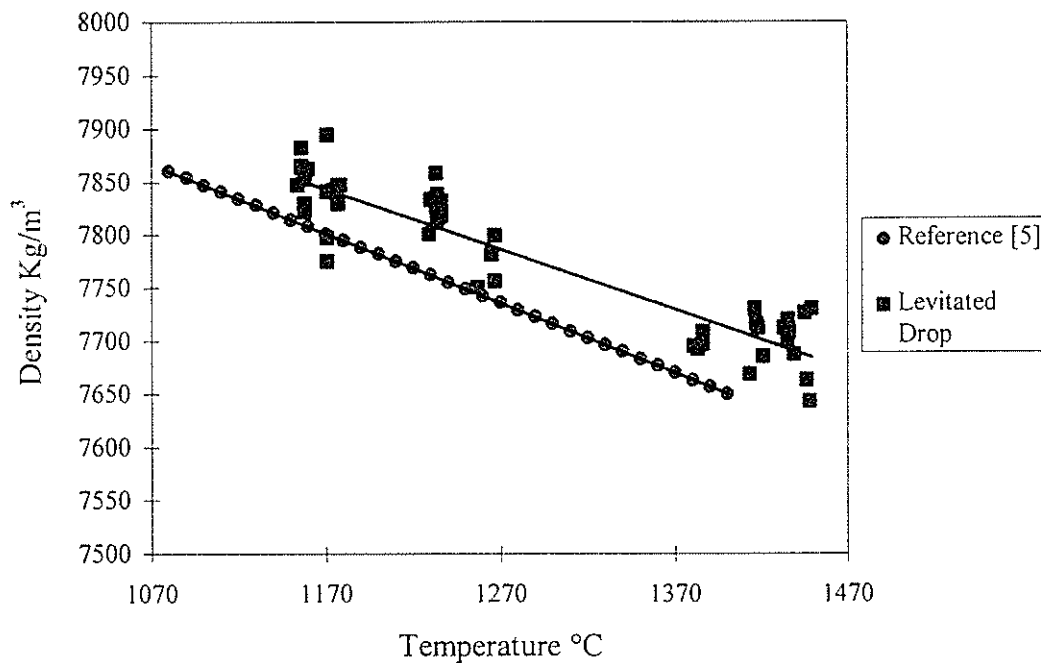


Figure 6 Density of Copper

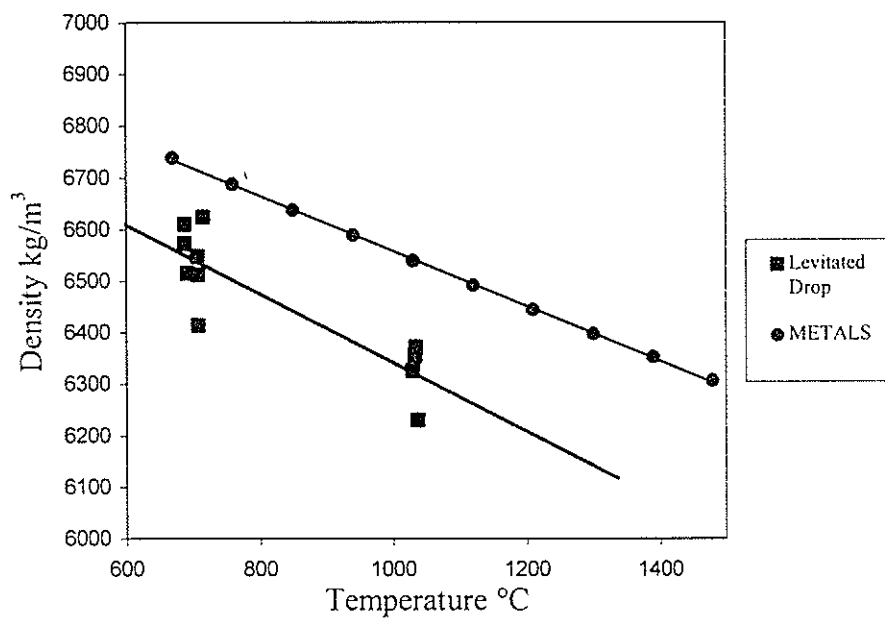


Figure 7 Density of Tin (temperature uncorrected)

To image samples at temperatures lower than 700°C additional lighting is needed. For the side views this is relatively simple. A fibre optic cold light source can be used to back light the drop, but from the bottom (the bottom needs to be lit so the top view can be seen) it is quite difficult due to the lack of space in the apparatus. A modification was made to the push rod assembly so that light could be passed through to the drop (Figure 8).

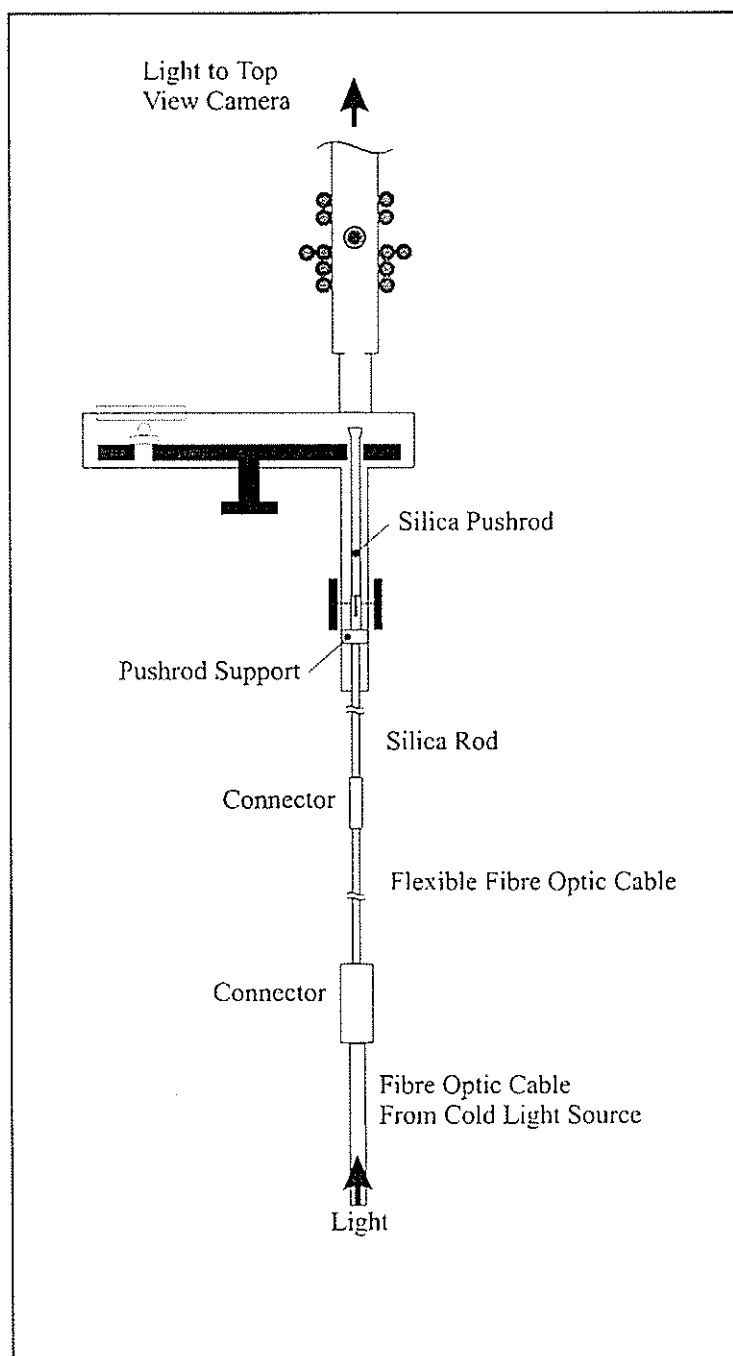


Figure 8 Schematic of push rod assembly for measuring low melting point alloys

The pushrod was made from quartz and the ends were polished flat and square. This was joined via a drilled metal connector to a perspex® rod, similarly polished. This rod passed through an o-ring seal out of the apparatus, and was used to raise and lower samples. Being perspex® it could withstand more mistreatment than a brittle quartz rod. A fibre optic cable was connected to the perspex®, so that when light was passed up the optic cable it was transmitted through the pushrod to illuminate the bottom of the sample. Figure 9 shows an example the top view of a drop which has been back lit. The test showed that it is possible to

image the drop at lower temperatures, but reflected light meant that the temperature could not be measured with any degree of accuracy.

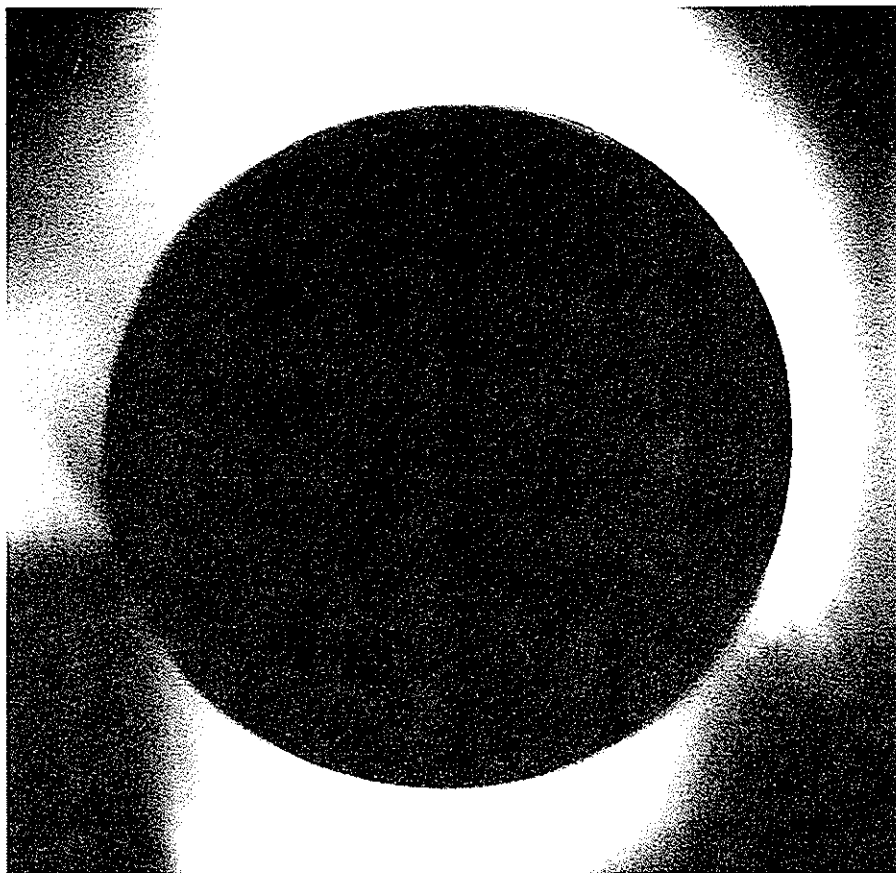


Figure 9 Top view of a levitated droplet which has been back lit. Shadowing in the corners is due to reflections within the square section tube.

7 TEMPERATURE MEASUREMENTS

Temperature measurements constitute a major source of uncertainty in the method due to lack of data available on the emissivity of liquid metals and alloys. In order to improve the accuracy of the measurements, a simple in-situ calibration method has been developed for optical pyrometers by the following methods:

- (a) By rapid cooling, the sample, a pure metal of the same generic group as the alloys under study, is allowed to supercool.
- (b) When the sample begins to solidify, the enthalpy of fusion causes the temperature to increase rapidly to the liquidus temperature (recalcescence) and this is recorded (T_{meas}).
- (c) This value (T_{meas}) is then compared with the known liquidus temperature (T_{ref}) and the temperature difference determined,

$$\Delta = (T_{\text{mea}}^{\text{liq}} - T_{\text{ref}}^{\text{liq}})$$

(d) Measured temperatures are then corrected using the relation:

$$T_{actual} = T_{meas} - \Delta$$

This procedure assumes that the ratio $d\epsilon/dT$ is constant and that fixing a single point will correct measurement errors throughout the range. Comparison of data obtained by other techniques which have used thermocouples for temperature measurement has not shown marked disagreement at high temperatures, which would be more likely should this assumption have been incorrect. However the effect of emission of metallic vapour at either high temperatures or in alloys containing volatile elements (e.g. Mn) on the two colour pyrometer is not known and could lead to small errors in temperature measurement.

In order to find a better way of making pyrometer measurements traceable, a technique is being developed to calibrate the pyrometers against reference thermocouples, and is shown in Figure 8. Two thermocouple wires are positioned below the molten droplet. The wires are too thin to couple with the induction heating and so they are not heated. When the power is turned off the droplet falls onto the wires fusing them and making a thermocouple. The output is then measured against the temperature reading of the pyrometer. As the thermocouple is made from certified material it can be assumed to be accurate and corrections can be made for the pyrometer. It has been found that the sample can often be re-levitated with the wires embedded allowing for more stable measurement conditions, and for temperatures to be varied during the measurement. If oxides form on the drop the apparent pyrometer temperature will change with emissivity but the actual temperature will not. The technique was initially developed using nickel, however, when tin was used it alloyed with the platinum wires. This meant a reading for only a very short period of time could be obtained.

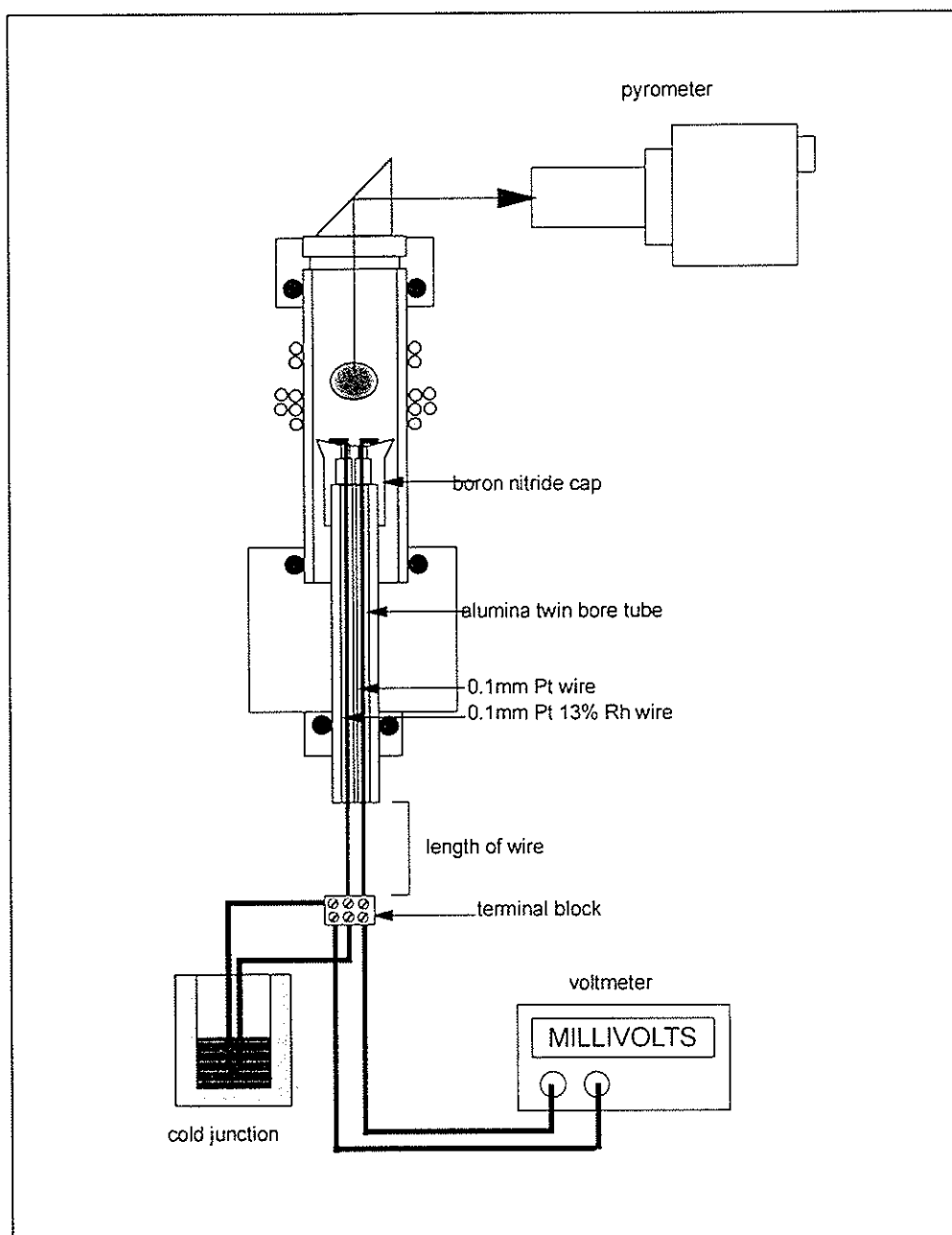


Figure 10 Schematic of calibration of pyrometers using the levitated drop method.

8 CONCLUSIONS AND FUTURE WORK

The project has shown that the technique can be used at very high temperatures, for a variety of metals and alloys. The method has also been shown to be feasible at lower temperatures although there are some weaknesses:

- 1 accurate temperature measurement is difficult due to
 - (a) lack of emissivity data for liquid metals
 - (b) low light radiation for pyrometer to measure due to low emissivity, small sample size and losses through windows/prisms
 - (c) reflections from back-light source.

- 2 imaging low emittance samples
- 3 vapour deposits on back-lighting source
- 4 oxidation of aluminium alloys due to high reactivity and surface-volume ratio
- 5 high speed oscillations can make imaging the drop edge difficult.

In the lower temperature range the most important commercial alloys are of aluminium. Due to its high reactivity it is almost impossible to prevent oxidation, and as the droplet is almost all surface this problem is maximised in levitation experiments. It is therefore suggested that more conventional methods, many of which are well suited to sub-1000°C measurements, are used for aluminium alloys.

Although minor improvements could be obtained by improved imaging and analysis this would entail much greater investment in equipment. Greater improvements could be obtained for levitation measurements in general with improvements in non-contact temperature measurement, either by improved emissivity data, or by the use of methods such as ellipsometry, or Laser Absorption Radiation Thermometry, a method currently under development at NPL.

9 UNCERTAINTY BUDGET

The uncertainty in this system is mainly due to the errors in the edge detection of the droplet, temperature measurement and loss of mass during a run.

9.1 ERRORS IN TEMPERATURE MEASUREMENT

Perhaps the most consistent source of error in the measurement is that of temperature. This is dependent on a knowledge of the emissivity / temperature relations of the wavelengths measured, of the material under study. Unfortunately these are largely unknown for the molten alloys, and will be dependent on the level of oxide present on the surface. Optical pyrometers usually have the ε / T slope fixed and calibration can only fix one point on the curve, usually at the known melting point of the metal. It is assumed that the temperature correction is constant over the whole temperature range. This may not be correct as there are usually no reference points available after the melting point. To get an idea of the uncertainty in the system due to the temperature measurement, an estimated error of $\pm 20^\circ\text{C}$ was applied to a density measurement of approx. 7000 kg/m^3 . The error in density is $\pm 0.35\%$.

9.2 ERRORS IN EDGE DETECTION

There are two areas of errors in edge detection, one in the calibration ball and the other in the drop. The source of error is due to the 'blurring' that occurs at the edge of the image, this makes it difficult to establish where the edge is. The 'blurring' can be due to the movement of the drop or due to the slightly different positions between the calibration ball and drop. The depth of field is very short and even slight movement can put the drop in or out of focus.

It is important that the CDD inside the camera does not receive too much light. This can cause 'flaring' of the pixels and make the image look larger than it really is. The amount of light received can be controlled by using filters, as described in this procedure.

A typical drop and typical calibration ball were used to calculate the uncertainty in density measurements due to edge detection errors. An average, minimum and maximum fit is taken for the calibration ball and used to calculate the maximum error in the density for each possible combination of fits.

Calibration Fit	Drop Fit	Density [kg.m ⁻³]	Volume x10 ⁸ [pixels ³]
Average	Average	4612	5.49457
	Minimum	4683	5.41181
	Maximum	4594	5.51673
Minimum	Average	4587	5.47787
	Minimum	4656	5.39673
	Maximum	4567	5.56195
Maximum	Average	4654	5.47787
	Minimum	4719	5.40224
	Maximum	4621	5.51673

The maximum error in density that can be obtained, with no change in mass, due to the uncertainty in edge detection is 3.3%

9.3 ERRORS DUE TO MASS LOSS

The average mass loss expected over a run is 0.0010g, this would increase the uncertainty in the density measurement by 0.2%. To keep this at a minimum the sample should be kept at temperature for a minimum time. A high mass loss of up to 0.0100g has been observed in metals with a low vapour pressure. This is an unusually high loss and would increase the uncertainty by 2%. Where there is a high mass loss, the time from when the sample becomes liquid is recorded. The mass can be based on either a linear relationship, between mass loss and time or a model based on the vapour pressure of the elements of the alloy.

10 TABULATED DATA

Table 1 Density of Iron

Temperature °C	Reference	Digital Cameras	Standard SLR's
1646			6862
1627			6961
1694			6939

Temperature °C	Reference	Digital Cameras	Standard SLR's
1627			6960
1627			7042
1627			7005
1656			6959
1775			6902
1775			6796
1550	7024		
1600	6981		
1700	6896		
1800	6810		
1662		6985	
1662		7027	
1664		6976	
1672		7009	
1667		7070	
1660		6970	
1570		7097	
1585		7140	
1587		7073	
1566		7027	
1562		6990	
1760		7020	
1767		6860	
1786		6870	
1784		6890	

Table 2 Density of Ti 6Al 4V

Temperature °C	METALS	Levitated Drop
1650	3947	
1700	3915	
1800	3854	
1693		3852
1835		3822
1666		3847
1819		3814
1835		3758
1770		3885
1770		3872
1693		3852
1670		3840
1695		3897

Temperature °C	METALS	Levitated Drop
1695		3901
1671		3890
1671		3890
1670		3840
1670		3889
1695		3897
1695		3901
1671		3997
1694		3921
1700		3900
1700		3900
1700		3890
1700		3899
1700		3898
1700		3964
1730		3897
1730		3883
1730		3837
1730		3925
1730		3833
1730		3818
1730		3902
1730		3911
1882		3730
1698		3841
1743		3913
1738		3912
1830		3759
1830		3810
1830		3739
1666		3847
1819		3814
1835		3758
1770		3878

Table 3 Density of Copper

Temperature °C	Reference	Levitated Drop
1156		7882
1154		7847
1156		7865
1156		7864

Temperature °C	Reference	Levitated Drop
1158		7852
1158		7828
1158		7829
1158		7822
1160		7862
1386		7708
1383		7692
1386		7697
1383		7695
1381		7695
1257		7750
1267		7756
1267		7799
1265		7781
1413		7668
1416		7730
1417		7716
1418		7712
1421		7685
1421		7695
1169		7877
1171		7797
1171		7775
1171		7894
1171		7841
1175		7842
1178		7847
1177		7829
1177		7847
1433		7712
1435		7720
1436		7708
1435		7699
1439		7687
1445		7726
1448		7643
1449		7730
1446		7663
1233		7858
1229		7800
1230		7833
1233		7827
1234		7820
1236		7817

Temperature °C	Reference	Levitated Drop
1234		7814
1234		7838
1236		7832
1080	7860	
1180	7795	
1280	7729	
1380	7663	

Table 4 Density of Tin

Temperature °C	Reference	Levitated Drop
692		6515
688		6610
708		6511
707		6547
708		6414
716		6624
688		6572
1034		6372
1029		6325
1037		6230
1033		6354
400	6896	
490	6843	
580	6790	
670	6738	
760	6687	
850	6637	
940	6533	
1030	6539	

11 REFERENCES

1. A.E. El Mehairy and R. G. Ward: 'A New Technique for the Determination of Density of Liquid Metals,' TransAm. Inst. Metall. Engrs., 1963,227, 1226-1228.
2. S. Shiraishi and R. G. Ward: 'The Density of Nickel in the Superheated and Supercooled Liquid State,' Canad. Metall. Quart., 1946, 3, 117-122.
3. K. C. Mills and R. F. Brooks: Material Science and engineering. A178 (1994) p77-81.

4. K. C. Mills, A. P. Day and P. N. Quested: Proc. of Nottingham University - Osaka University Joint Symposium held Nottingham, Sept 1995.
- S. Watanabe and T. Saito: J. Japan Inst. Metals, 35 (1971), 554; Trans. JIM, 13 (1972), 186.