1
Introduction

1.1.Background

Temperature is one of the most measured physical quantities in the modern world. From measurements of near ambient temperatures, for example the human body, meteorology and cooking, to very high temperatures measured in industrial production such is iron and steel, glass, ceramics and nuclear fuel production to very low temperatures present in fundamental research in basic physics, many temperature measurements are performed everyday using many different techniques. Indeed, many scientific and technological advances were only possible due to the precise control and measurement of temperature and, in particular, modern efficient industrial production largely hinges on having access to reliable temperature measurement and control.

Temperature measurement throughout the world is in accordance with the International System of Units (SI). The SI [1] consists of seven base quantities (e.g. mass, time) with seven associated base units (e.g. the kilogram, the second), which can be seen in Table 1, and a number of derived units such as acceleration, area or force. One of these seven base quantities is thermodynamic temperature, whose defining unit is the kelvin (K). The kelvin is formally defined as "The kelvin, unit of thermodynamic temperature is the fraction 1/273,16 of the thermodynamic temperature of the triple point of water[1] (where solid, liquid and vapor phases coexist in equilibrium at unique temperature and pressure) [2]. The kelvin is named after the British physicist William Thomson, ennobled as first Baron Kelvin of Largs. The foundation of all reliable temperature measurement starts from this definition.

[1] http://www.bipm.org/utils/en/pdf/MeP_K_Technical_Annex.pdf - corrections for isotopic composition of the water should be applied with respect to SMOW (Standard Mean Ocean Water)

Table 1: Base units of the International System of Units (SI)

Base quantity	SI base unit	
	Name	Symbol
Length	metre	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	Mol
Luminous intensity	candela	Cd

In practice, most temperature measurements are performed using contact thermometers such as those based on the varying resistance of platinum (or other wire) or the thermovoltage generated when two dissimilar wires are joined at the tip and placed in a temperature gradient (a thermocouple). It is also possible, and indeed it is common in industry, to perform non-contact temperature measurement based on thermal radiative emission. This method of measuring temperature has a long history, from fundamental studies of Planckian emission in the late 19th Century, to many common industrial applications including iron and steel production, materials and chemical processing. It has also played a fundamental role in the realization and dissemination of successive international temperature scales, at least at high temperatures. Radiation thermometry is attractive in many challenging temperature measurement situations because it is a noncontact, nonintrusive and fast technique. Thermal radiation is governed by the fundamental physical laws established over one hundred years ago by Kirchhoff, Stefan, Boltzmann, Wien, and, in particular, Planck. These laws directly link emitted blackbody radiation, total or spectrally resolved, to the thermodynamic temperature of the emitting source. If the emitter is a good blackbody, of uniform temperature, then the material of construction of the blackbody is irrelevant as the thermal emission is solely dependent upon its temperature [3].

However, in practice, radiation thermometry is subject to a number of uncertainties associated with, for example, surface emissivity and environmental effects such as absorption by dust or smoke and reflected thermal radiation. Nevertheless, the widespread use of non-contact thermometry in industry is a testimony to its usefulness, with many of these problems mitigated by design of the measurement situation.

One example illustrating the importance of a precise high-temperature measurement for engineering processes is found in the development of materials, and in particular turbine blade materials of airplane jet engines. Continued improvement is required to increase the energy efficiency which is achieved by running the hot zone of the engine at increasingly higher temperatures. However, although the efficiency is increased, the thermal stress on the materials and new alloys used in the engines increases – driving the requirement for new alloys and materials. One such has been developed by Rolls Royce, UK, but the materials require thermal annealing at a temperature of approximately 1300 °C and must allow deviation from the maximum temperature by less than 3 °C, ideally only 1 °C. Without the advent of new high-accuracy high–temperature fixed-points, a small deviation would not be possible at these high temperatures.

Although the above example relates to contact thermometry, it nevertheless demonstrates the strong need for accurate temperature measurements in the high temperature range between 1000 °C and 3000 °C. The inherent limitation of the high-temperature part of the actual temperature scale, the ITS-90, is the general lack of suitable high performance high-temperature fixed-points. This is in contrast to the temperature range below the freezing temperature of Copper (1084,62 °C) [the highest temperature fixed point defined on the ITS-90], where a large number of temperature fixed-points, represented by the phase transition of very pure elements, enables an interpolation function for the calibration of (contact) thermometers assuring lowest measurement uncertainties. However, for temperatures above the freezing temperature of Copper, the uncertainty in the temperature scale realisation is principally limited by the absence of stable and reliable temperature high-temperature fixed-points. Above that temperature the scale, for non-contact thermometers, is presently extrapolated from the highest fixed-point (usually Ag or Cu freezing points) during calibration leading to a measurement uncertainty of several °C at 3000 °C. For thermocouple calibration, secondary fixed points based on wire-bridges of Pd or even Pt are available, but generally not as crucibles because no suitable containment material is available, yielding larger uncertainties.

Resolving these inherent limitations of high-temperature measurement requires the development and characterization of novel fixed-point materials in the temperature range above the freezing point of copper. Such materials have become recently available, these are high-temperature fixed-points made from metal-carbon (MC) eutectics. These show unique potential to facilitate primary scale realisation and dissemination. Such fixed-points, if ingots are made in pure graphite crucibles, are innately independent from contamination from the crucible as the crucible itself is made from carbon which is also part of the eutectic alloy. Such fixed-points show a unique melting and freezing temperature, they are not subject to drift, are robust and can easily be transported. Table 2 shows some of these fixed-points [4, 5].

Table 2: Metal-carbon and metal carbide-carbon eutectics and their approximate fixed-point temperature

Eutectic	Approximate temperature/K	Approximate temperature/° C
Metal-carbon		
Fe-C	1426	1153
Co-C	1597	1324
Ni-C	1602	1329
Pd-C	1765	1492
Rh-C	1930	1657
Pt-C	2011	1738
Ru-C	2226	1953
Ir-C	2565	2292
Re-C	2747	2474
Metal carbide-carbon		
B_4C-C	2659	2386
δ(MoC)-C	2856	2583
TiC-C	3032	2759
ZrC-C	3155	2882
HfC-C	3458	3185
Metal carbide-carbon peritectic		
Mn_7C_3-C	1604	1331
Cr_3C_2-C	2099	1826
WC-C	3022	2749

The implementation of such metal-carbon fixed-point cells in any future temperature scale demands careful investigation to guarantee reproducible manufacture and robustness. Additionally, the temperature of the phase transformation must be proved to be repeatable over time and, in particular, determined with the lowest measurement uncertainties. Work on characterisation of MC eutectics is embedded in a worldwide project on improving the high-temperature part of the ITS-90. In relatively recent years, in Europe, this research was bundled within the European Union funded project "Novel high temperature metal-carbon eutectic fixed-points for radiation thermometry, radiometry and thermocouples - HIMERT" [6]. Partners cooperating within the project were the National Physical Laboratory NPL (UK), Laboratoire National de Metrologie et d’essais – Institut National de Métrologie/ Conservatoire National des Arts et Métiers LNE-INM/CNAM (France), Physikalisch-Technische |Bundesanstalt PTB (Germany), Universidad de Valladolid (Spain) supported by a collaboration with the National Metrology Institute of Japan (NMIJ) (Japan).

The overall objective of the work on these high temperature fixed points will be to have them recognized as stable reliable references for realization and dissemination of thermodynamic temperature or ITS-90.

1.2. Motivation for this research

For many years, the International Temperature Scale of 1990 (ITS90) above the silver point has been realized by using Planck's law in ratio form. A reference blackbody at the freezing point of silver, gold or copper provided the foundation of the scale. This coupled with a spectrally well characterized radiation thermometer and a variable temperature radiance source allowed the ITS-90 to be established. However, to assess the quality of the realization the scales should be compared among National Metrology Institutes (NMIs). This has been performed through the use of high stability tungsten strip lamps [3,7]. However, these are no longer suitable as comparison artefacts, partly because they no longer cover the temperature range institutes operate over, the target size is very restricted (generally 1.5 or 3 mm), they are very fragile and they are not blackbodies and so can only be used at the wavelength of calibration. Finally, and possibly most importantly, as the calibration measurement capabilities (cmcs) of NMIs have greatly improved during the last decade, these lamps no longer have the stability required to validate cmcs. This was particularly the case observed in the last Consultative Committee for Thermometry (CCT) key comparison of the Bureau International des Poids et Mesures (BIPM) in this temperature range, the CCT-K5 [8].

This problem motivated this study into the development of a new comparison artifact, which could overcome the problems encountered when using lamps but which would be robust enough to be shipped by ordinary mail to the participating NMIs, without the need to be hand carried. This study focuses on understanding the effect of doping high temperature fixed points (HTFPs), initially of Co-C with more extensive studies performed with Ni-C.

The problem with using HTFPs is that their temperature is increasingly well known so that the essential blindness aspect of a key comparison is missing. Therefore, a means of adjusting the temperature to an unknown one, whilst retaining the performance of the HTFP is required. In this thesis it is anticipated that by introducing a small amount of dopant into the metal of the fixed point, performance is retained but the temperature is adjusted. It is hoped that the work performed here, through developing high performance comparison artefacts with an unknown realization temperature, that the scale realization and measurement capabilities of top level NMIs will be able to be evaluated, but avoid bias in the results.

1.3. Scope of the work

The main objective of this work is to design, construct, fill and measure eutectic cells adequately doped with selected elements in a way to change its transition temperature by some tenths of degrees Celsius, evaluating its stability in time. A bilateral comparison with a leading NMI is also envisaged to proof the concept of using such artefacts for scale comparisons.

Firstly, the graphite type for the crucible to contain the metal-carbon alloy had to be selected with desirable properties such as high purity, high heat conductivity and small porosity. The design of the graphite parts for the fixed point cell assembly followed by the construction of the graphite parts were the next steps. The selection of the metal for the eutectic alloy was made considering the availability of high purities in powder form, the price and the transition temperature. The practical consideration of limiting the MC eutectic temperature to lower than that achievable by the available furnaces at Inmetro was also required. This was necessary to enable the graphite to be purified, the cells filled and for realizing the fixed points.

The next step was to select the dopant for the eutectic alloy. This should present some properties such as crystal structure, atomic radius and density close to the ones of the base metal, except the melting temperature. To aid the selection, the effect of doping on the transition temperature of the eutectic alloy was simulated using the software Thermo-Calc with appropriate databases. These calculations gave an estimate of the amount of dopant necessary for a determined temperature change in the metal-carbon eutectic alloy. Also, the measurements showed how reliable, or otherwise, it was to rely on modeling to predict shifts in transition temperature.

A procedure had to be developed to investigate how the doping changed the fixed point temperature. This was done by making a blackbody crucible of the pure MC fixed point and then making cells with different dopant levels. Comparing the two allowed differences caused by doping to be accurately determined.

With all this information, it was possible to start filling the cells. A procedure had to be developed to do this, as well as for doping with the correct amount of dopant. When the cells were filled, the measurement of the transition temperature was the next step. The point of inflection of the temperature versus time curve was used, as this is known to be a stable feature of the melting curve of a MC eutectic. This part of the project also included studies into the long term stability of the transition temperature of the metal carbon alloy, and also the temperature difference with respect to the metal-carbon eutectic cell without any dopant.

Finally, to demonstrate the suitability of the cells as comparison artefacts it was necessary to compare the transition temperatures of the doped eutectic cells constructed and measured at the Pyrometry Laboratory of Inmetro, with those obtained for the same cells by another National Metrology Laboratory. For this purpose, two doped cells were sent to the National Physical Laboratory (UK) to have their transition temperature determined. This laboratory did not know beforehand what these temperatures were; only a general indication was given. With the results achieved, it was clear that doped cells are excellent comparison artefacts for demonstrating scale realization and equivalence.

1.4.Structure of the thesis

This thesis is organized in nine chapters and one annex, with this first one giving an introduction of the work.

The second chapter describes the principles of temperature measurement, including the necessity of a practical temperature scale in place of thermodynamic measurements, the latest temperature scale adopted by the BIPM and an outline of the most common temperature sensors used at the present time.

The third chapter deals more specifically with radiation thermometry, giving information about the current state of the art of the technique. The use of the high temperature metal-carbon eutectic cells as fixed-point references for radiation thermometry and the type of radiation thermometer used to perform the measurements in this work will be described.

The fourth chapter deals with the thermodynamic simulation of the effect of adding a certain quantity of dopant to the metal-carbon eutectic cell in its transition temperature. For these simulations the software Thermo-Calc, which can perform this task with the aid of thermodynamic databases and mathematical and numerical tools, was used.

The fifth chapter contains detailed information on the experimental methods used for the design and construction of the cells, the determination of the point of inflection of the melting point curve of the metal-carbon eutectic cells and also some preliminary results taken for the cobalt-carbon eutectic system. This type of cell was superseded in favor of the nickel-carbon system – as explained in this chapter. It is also shown the revised design of the fixed-point blackbody cell, which was required to improve robustness.

The sixth chapter presents the results of the temperature measurements of the Ni-C and the two Ni-C-Cu eutectic cells (doped with different amounts of Cu) are reported. A comparison of the results produced by the simulation and by the experiments is discussed. Experiments are reported concerning the long term stability of the melting temperature of the doped Ni-C-Cu eutectic cells.

The seventh chapter presents the measurement results of the Ni-C-Sn eutectic cells, following the pattern of the previous chapter.

In the eighth chapter the results of an interlaboratory comparison between Inmetro and NPL are presented, where two cells Ni-C-Cu with two different dopant concentrations were measured at both institutes. Measurements were repeated at Inmetro to assess the stability due to transport of the artefacts.

In the ninth chapter, there is a detailed description of the uncertainty of the measurements performed for this thesis.

Finally, in the tenth chapter, some conclusions of the present work and suggestions for future work are presented.