PROGRESS IN HIGH-TEPMERATURE FIXED POINTS USING METAL-CARBON EUTECTICS

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ABSTRACT

A review is given on the progress in the high-temperature fixed points using metal-carbon eutectics. The development of the fixed points consists of three stages, evaluation of the repeatability for a single cell, evaluation of the reproducibility among different cells, and finally, the determination of the fixed-point temperature. Repeatability for a single cell has been confirmed to be well within 0.1 ^{o}C by several national laboratories, and the fixed points have already been proven to be capable of replacing the standard lamp as transfer standard. Comparison between cells from NPL and NMIJ has revealed a difference of almost 1 ^{o}C. To investigate the cause, melting and freezing plateau shapes of the high-temperature fixed-points were investigated in temperature uniform furnaces, which showed them to be strongly affected by the material purities only. Extension of the fixed-point temperature to above 2500 ^{o}C, and utilization of the fixed points for improvement of the high temperature scale are also discussed.

1. INTRODUCTION

In the two years' time since their first introduction, many standard laboratories have become involved in the development of the metal-carbon eutectic fixed points, which may enable 9 fixed points in the temperature range from the copper point to 2500 ^{o}C. At the TEMPMEKO meeting in June this year, there were 8 presentations related to this subject, involving 9 institutes as author or co-author. This document summarizes two papers presented by the authors at the TEMPMEKO[1,2], and aims to review the current state of development of the high temperature fixed points using metal-carbon eutectics, and to show future demands and prospects.

2. REPRODUCIBILITY OF THE FIXED POINTS

In a preliminary investigation previously reported [3,4,5], the fixed points showed that repeatability for the same cell of 100 mK in standard deviation could generally be achieved for the melting plateau. The evaluation was done using furnaces with not necessarily the best temperature uniformity and, for the fixed points above 1500 ^{o}C, with small-size crucibles (outer diameter of 24 mm) in a graphite tube furnace with a window (Chino, model: IR-R8). The observed melting and freezing plateaus were never flat. It was of interest how small the repeatability would be and how flat the plateaus would become in optimized temperature uniformity using full-size crucibles.

Therefore, a more precise evaluation is in progress at the NMIJ using furnaces with 3-zone temperature control to realize better temperature uniformity, and full-size crucibles (outer diameter of 46 mm). In these improved conditions, the melting plateaus showed repeatability better than 70 mK in standard deviation. The plateau shapes also showed improvement and became flatter. However, they were never as flat as in pure-metal fixed points. These are reported in detail in [2], which is summarized in the next section. The reason why the plateau is curved is interesting to consider because this will tell us which part of the curve corresponds to thermal equilibrium.

In the mean time, the small-size crucibles were sent to other national metrology institutes and their performances were tested in different thermal conditions. In the NML and in the KRISS, they were tested in windowless graphite tube furnaces (both Thermogage, model 48). Similar performances as in the Chino furnace were observed [6]. In the VNIIOFI, the small-size crucibles were placed in a graphite furnace using pyrolytic graphite (model: BB3200) for improved temperature uniformity [7,8]. Repeatability of 0.01 % or better, equivalent to 30 mK, was achieved.

The international collaborative investigation is now in the next stage: evaluating the reproducibility between different cells with different crucible designs, with different material sources, and different material purity. The comparison between the NPL and the NMIJ, described in detail in another paper at the TEMPMEKO[9], and also in this meeting[10], revealed that the differences were much larger than their individual repeatability, the largest difference being almost 1 K. The reason for these discrepancies is being investigated, whose preliminary results are presented in the following section.

3. MELTING AND FREEZING PLATEAUS OF METAL-CARBON EUTECTIC FIXED POINTS

As mentioned in the previous section, the plateau shape for the metal-carbon eutectics were curved, and were never entirely flat. Many causes could be assumed for this, such as temperature non-uniformity of the furnace, separation of the two materials by difference in density, effect of non-planer interface of the solid and liquid of eutectics, formation of primary phase carbon, or effect of impurities. To find out which of these were actually having effect, the melting and freezing plateau shape of the high-temperature fixed points were investigated in detail.

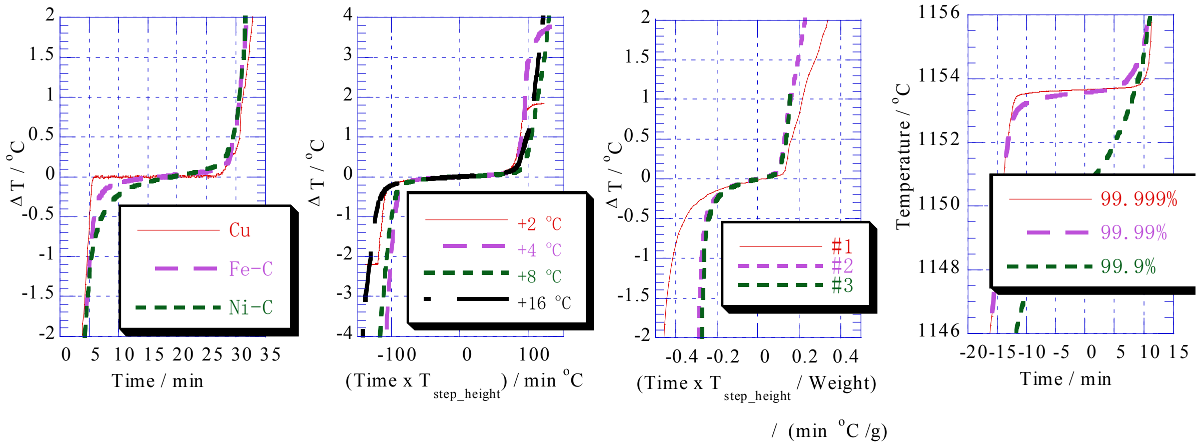
Three-zone furnaces, which are able to control the temperature distribution precisely, were used in the investigation. Melting and freezing plateau shapes were compared 1) between different material, 2) for different melting / freezing rates, 3) for crucibles with different design and sizes, and 4) for material with different nominal purities.

First, melting and freezing plateaus were compared among Cu (99.999%), Fe-C eutectic (99.999%), and Ni-C eutectic (99.996%) with the purity of the metal quoted by the supplier shown in the parenthesis. The crucibles used were all of the same size and design (labeled #2 below). The melting plateau shape with optimum temperature distribution and the furnace temperature step change from T_{step_height} below to T_{step_height} above the equilibrium temperature, with T_{step_height} = 8 ^{o}C, is shown in Fig. 1 a). It is apparent that, even though better temperature uniformity has improved the flatness of the plateaus, the melting and freezing plateaus of metal-carbon eutectics are still quite rounded, which is in clear contrast to the extremely flat plateau of the copper.

Next, melting plateaus were observed for different T_{step_height}'s so as to clarify the effect of melting rate on the plateau shape. The larger the T_{step_height}, the shorter the plateau becomes, since the plateau duration is inversely proportional to the T_{step_height}. Therefore, the plateau shape was compared after the time scale was normalised by the inverse of T_{step_height}. In Fig 2 b), the plateaus for various T_{step_height} are shown for Fe-C eutectic. The plateau shape is seen to fall upon each other, and the plateau shape is not affected by the melting rate. It can be said from these results that the plateau shape is independent of the melting and freezing rate.

The effect of crucible size was investigated. Using Pt powder of the same purity of 99.99 %, three crucibles of different sizes, labeled #1, #2, #3, were filled. The ratio of the metal weight for the three cells was roughly 1:4:8. Pt powder filled in the #2 and #3 crucibles came from the same material lot but the powder filled in the #1 crucible came from a different lot. The plateau duration is proportional to the metal weight for the same metal-carbon eutectic. Therefore, the time scale was normalised by the metal weight. It is seen from Fig. 1 c) that #2 and #3 Pt-C cells show no dependence on the type of crucibles and the #1 Pt-C cell also almost showed the same plateau shape as #2 and #3 cells. From these observations, it can be said that the plateau shape is independent of the crucible shape and size.

To clarify the effect of impurities for the plateau shape, Fe-C eutectics were investigated using different nominal purity materials. 99.999%, 99.99% and 99.9% nominal purity materials were filled in #2 type crucibles. In Fig. 1 d), very flat melting plateau is shown for 99.999% purity Fe-C eutectic, which is in clear contrast to the poor melting plateau of 99.9% purity cell. Later, chemical analysis was performed to check the true purity, which revealed the 99.9% nominal purity material to be merely 99.3% pure. Even so, from this result, it is clearly shown that Fe-C eutectic is very sensitive to impurities.



a) material type   b melting rate   c) crucible size #1:#2:#3≅1:4:8   d) material purity

Fig. 1 Melting plateau shape dependence on various parameters

In the above, the melting plateau shape showed dependence only on material purity. The same was found for the freezing plateau shape, except for the dependence of the freezing point on freezing rate, which is characteristic of eutectics. The results seem to cross out all causes assumed for the curved plateau shape, and leave impurity effect as the only possible cause.

The metal-carbon eutectics appear to be more susceptible to impurities than pure-metal fixed points, as shown in Fig 1. a), although there is still no clear explanation as to why this should be so. Fig. 1 d) shows that the melting point, evaluated at the inflection point of the curve, can be affected by impurities, and could cause the discrepancy between the NPL and NMIJ cells described in the previous section. Method to evaluate the effect of the impurities, or to correct for this effect and the method to evaluate the uncertainty of this correction, should next be investigated. On the other hand, how to obtain high purity material, and how to assess its purity becomes another important issue.

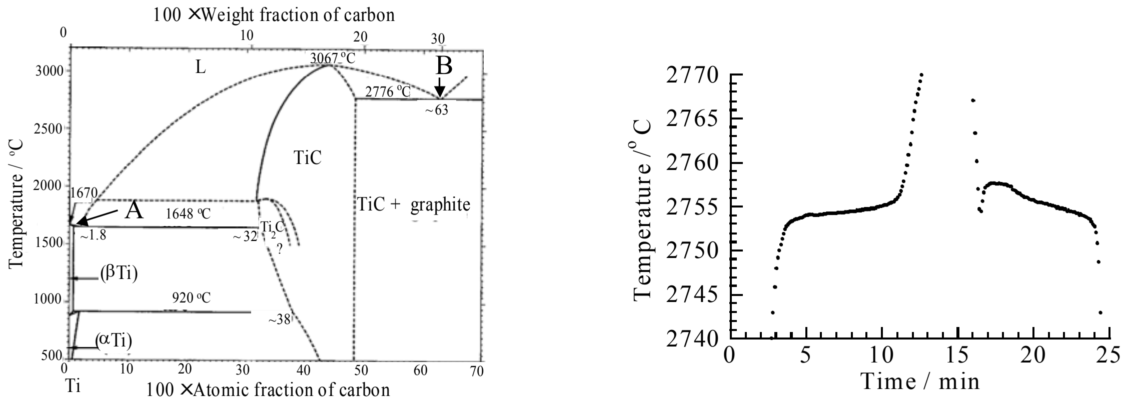
4. POSSIBILITY OF FIXED POINTS ABOVE 3000 K

There are many other metals that also show high melting points. So, the natural question to ask is "How about other metals?" "Why can't other metals work as fixed points in graphite crucibles?" The authors believe the answer to this question is yes; there are other possible combinations.

The ten metals with high melting point under investigation as metal-carbon eutectic points are the ones that show the simplest binary phase diagram with carbon. For all the others, carbides are formed, which makes the binary phase diagram complex. For instance, Ti forms TiC, which has melting temperature of 3067 °C, according to literature [11]. The phase diagram (Fig 3) tells us that TiC forms eutectic with Ti (marked A in the figure), and with graphite (marked B). In order for the similar principle to work as in the metal-carbon eutectics, one component of the eutectic must be the crucible material. Therefore, the possible material combinations are Ti-TiC eutectic in Ti (or TiC) crucible, and TiC-C eutectic in C (or TiC) crucible. The former is not easy to realize readily, for reaction between the crucible material and the furnace material (which is normally graphite) is hard to prevent. On the other hand, TiC-C eutectic in graphite crucible involves no additional technical improvements (except for a higher temperature furnace), and is of more interest, because the eutectic point is higher than all the metal-carbon eutectic points and is above the 3000 K mark.

A simple preliminary experiment was done to see if the plateau could actually be observed. A small crucible of 45 mm length and 24 mm outer diameter containing 15 g of the eutectic material (30 weight % of carbon, according to [11]) was placed inside an ultra-high temperature vertical furnace. A plateau observed by a radiation thermometer viewing from the top through the quartz glass window is shown in Fig. 3. Despite the extremely poor temperature uniformity of the furnace, melting and freezing plateaus were clearly observed.

This demonstrates the possibility of a new series of fixed points using metal carbide-carbon eutectics. Among these are ZrC-C eutectic at 2927 ^{o} C and HfC-C eutectic at 3180 ^{o}C, according to [11]. Further investigations to see if the metal carbide-carbon eutectics show reproducible plateaus, to see if the plateau shapes are any better than the metal-carbon eutectics, and to test if fixed points above 3000 ^{o}C can be realized, could lead to new developments in ultra-high-temperature standards.



a) Ti-C binary phase diagram

b) Melting and freezing plateau

Fig. 2 TiC- C eutectic fixed point

5. UTILIZATION OF THE FIXED POINTS FOR HIGH-TEMPERATURE STANDARDS

5.1 Temperature scale realization, dissemination and comparison

The high-temperature fixed points can serve the temperature standards in various ways depending on the level of quality achieved.

1) It is shown in section 2 that the fixed points show sufficient repeatability for each cell. If long term stability is also proven, it is safe to say that the fixed points can be used to maintain the ITS-90. The fixed-point cells, individually calibrated, can also be used as transfer standards for disseminating the scale to industry. They can also serve as transfer standards for temperature scale comparison. In a sense, it will replace the standard lamps. Compared to lamps, the temperature range will be extended. There will be no need for hand carry, no correction for wavelength and much smaller correction for the SSE (size-of-source effect).
2) If, in addition, the fixed points show reproducibility between different cells, then the cells can serve

as secondary fixed points to calibrate radiation thermometers. The calibration will be by interpolation up to the highest fixed point and by extrapolation above that using the fixed-point temperatures predetermined on the ITS-90 as by the absolute radiometry along with its uncertainty. Techniques using fitting equations [12] are already being used below the copper point. The exactly same technique can be applied, while the temperature range is extended.
3) If the fixed points are eventually adopted as defining fixed points in the future revision of the ITS, the uncertainty of temperature scale realization will be reduced dramatically, for the exact temperature values are assigned to each fixed point by definition.

In the international collaborations mentioned in section 2, temperature scales realized independently at various institutes were compared at the fixed points, and were found to agree within each others' uncertainties[6,8,9,10]. This proves the fixed points are already of level 1) and are capable of acting as transfer standards for temperature scale comparison.

5.2 Temperature scale fitting using the high-temperature fixed points
Now, a natural question to ask is, is it really necessary to make use of all of these fixed points for radiation thermometer calibrations? If not, then, how many do we need, and which ones? Simulated calculations were made in an attempt to answer these questions. The procedure of the simulations is as follows. Each fixed point was assumed to have the same uncertainty of 0.1 °C. The temperature uncertainty in the resulting scale fitting keeping the uncertainty for the other fixed points to be zero was calculated for the interpolation and extrapolation temperature ranges. Treating each fixed-point uncertainty statistically independent, the combined uncertainty of the scale fitting was calculated. The Hattori-Sakuma equation adapted to Planck's form [12] was used as the fitting equation.

The uncertainty was calculated for four cases. Three cases used the copper point as the lowest and the Re-C eutectic point (2474 °C) as the highest calibration points. The first used one additional fixed point, the Pt-C eutectic point (1738 °C). The second used two additional fixed points, the Pd-C (1492 °C) and Ru-C (1953 °C) eutectic points. The third used three additional fixed points, the Pd-C, Pt-C, and Ir-C (2290 °C) eutectic points. The fourth case also used the copper point and the Re-C eutectic point, and for the additional third fixed point the Al point (660 °C) was used. A measurement wavelength of 900 nm for the radiation thermometer was assumed for the fourth case. For the rest, a 650 nm measurement wavelength was assumed.

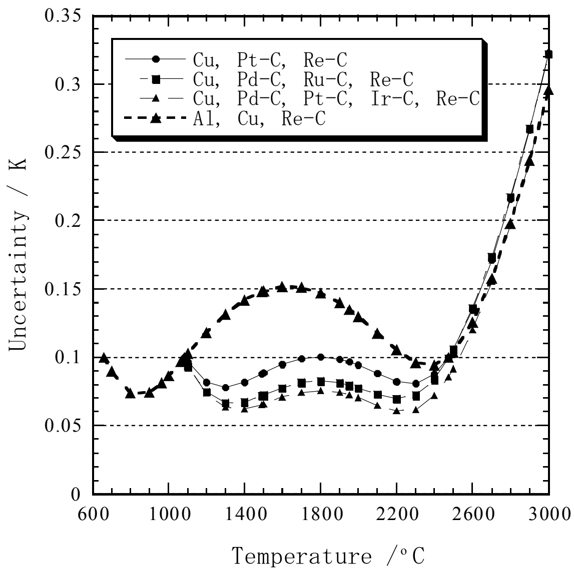


Fig.4 Calculated temperature scale uncertainty realized by various selections of fixed points, assuming 0.1 °C uncertainty for each fixed point

The simulation results of the temperature scale uncertainty are shown in Fig. 4 [13]. The results show that the use of two or three additional eutectic points to the copper point would be sufficient to suppress the scale uncertainty in the interpolation temperature range to within the uncertainty of the fixed points. Redundancy in the fixed points would reduce the uncertainty in the interpolation range, but would not improve in the extrapolation range. It is also shown that, the choice of 900 nm wavelength radiation thermometer and one additional eutectic point to the Al and Cu points could be another option. The resulting uncertainty is much smaller than the current ITS-90 realization uncertainty, which is generally 1 to 2 ^{o}C above 2000 ^{o}C. A more detailed investigation by Saunders is presented at this CCT meeting[14].

It should be noted that for these simulations, all fixed points were assumed to have the same uncertainty of 0.1 ^{o}C. If some fixed points prove to be superior in performance than others, being easier to obtain higher purity material, for instance, then this should be taken into consideration of fixed-point selection. Although the interpolation is expected to be robust to nonlinearity effect of the radiation thermometers, this effect should also be taken into consideration when choosing the number of calibration points.

The large number of possible high-temperature fixed points offers a variety in the choice of temperature scale realization and dissemination schemes. On the other hand, high temperature facilities and high-purity fixed-point materials require a relatively large amount of investment compared to conventional fixed points. Cost effectiveness should be a major point to consider in the choice of the scheme.

6. CONCLUSIONS

The application of the metal-carbon eutectic fixed points is not restricted to high-temperature scale realization, maintenance and dissemination of the ITS-90. The CCT recommendation of 1996 [15], which encouraged national standards laboratories to work to develop high temperature fixed points above 2500 K with reproducibility better than 100 mK, was based on the report of the joint working group of the CCT and the Consultative Committee of Photometry and Radiometry (CCPR), which was working on the measurement of thermodynamic temperature of high temperature blackbodies [16]. The high-temperature fixed points can be used as the reference point to link and compare various thermodynamic temperature measurements.

The recent developments in the high-temperature fixed points have all happened in the last two years since the method of using metal-carbon eutectics as fixed-point material was introduced. This speed of progress is an indication of the ease of implementation of this technique, and is also an indication of its practicality. The complexities usually encountered at high temperatures that arise from material reactiveness have been avoided by making possible the use of graphite crucibles.

For further development of the high-temperature fixed points, international involvement is essential. To determine the fixed-point temperatures with uncertainties as small as possible, and to prove the equivalence of cells of different origin, more international comparisons need to be conducted. Discussions have already begun on how to implement the high-temperature fixed points for the improvement of the future high-temperature scale[17,18].

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