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Experimental Investigation of the Cr_3C_2–C Peritectic Fixed Point

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Abstract The Cr_3C_2–C (1,826°C) peritectic point was investigated for its performance as a high-temperature fixed point. Dependence on the impurity content was observed, although it was less severe for the higher of the two equilibrium temperatures obtained with the same cell, the Cr_3C_2–C peritectic point, than for the lower, the Cr_7C_3–Cr_3C_2 eutectic point. Thermal history had an effect on the melting plateau duration, but not on the point-of-inflection temperature nor on the melting range. The melting rate had no apparent effect. The repeatability evaluated as the standard deviation of the repeated melting plateaux within a day was 20 mK for the Cr_3C_2–C peritectic point, while for the Cr_7C_3–Cr_3C_2 eutectic point, this was 210 mK. For both the Cr_3C_2–C peritectic and the Cr_7C_3–Cr_3C_2 eutectic, the freezing plateaux often showed deep supercools, which made them unsuitable for use. The observed good repeatability shows the peritectic-point performance to be comparable to the best MC-eutectic high-temperature fixed points investigated so far. The insensitivity to thermal history constitutes an important and practical advantage. The low price of chromium is a clear benefit as compared to Pt–C (1,738°C) or Ru–C (1,953°C) eutectic points, the M–C eutectic points in this temperature range.

Keywords Chromium carbide · Eutectic · Fixed point · High temperatures · Peritectic · Radiation thermometry · Temperature standards

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1 Introduction

In this paper, we describe the experimentally evaluated fixed-point performance of the Cr_3C_2–C peritectic point (1,826°C), as a follow-up to an earlier investigation reporting the first observations of melting and freezing of metal carbide–carbon (MC–C) peritectic points [1]. In another paper in these proceedings by the authors, the Cr_3C_2–C peritectic point is studied for the purpose of understanding the peritectic reaction involved [2]. A third paper describes the investigation of the WC–C peritectic point (2,749°C) [3].

The MC–C *peritectic* systems are different from the M(C)–C *eutectic* points [4] in that they show plateaux at two different temperatures. For example, the Cr–C system has two transitions, the Cr_3C_2–C peritectic point (1,826°C) and the Cr_7C_3–Cr_3C_2 eutectic point (1,742°C). This is an indication that there is still a liquid phase remaining even when the freezing at the peritectic phase transition appears complete. In [2], microstructure analysis showed two distinct domains in the ingot, one rich in carbon and the other rich in chromium. Comparison with the observed plateaux indicates that the carbon-rich portion is the solid formed when the Cr_3C_2–C peritectic freezes, and the chromium-rich part forms when the Cr_7C_3–Cr_3C_2 eutectic freezes. The plateau durations of the two transitions were clearly related to the ratio of volume of the two domains. In this paper, we report experimental results of the melting plateau's dependence on material purity, thermal history, and melting rate and discuss the fixed-point performance in relation to the investigations reported in [2].

2 Measurement Setup

2.1 Fixed-point Cells

Three cells of different purities were prepared for the current investigation. The material information is summarized in Table 1. The chromium powders were mixed with graphite powders of 99.9999% nominal purity (supplied by Johnson & Matthey). The crucible design is the same as in [2]. The graphite crucibles were purified to better than 99.9995% purity by the manufacturer (SGL Carbon). The filling of the cells was performed according to the non-porous filling method without the C/C sheet wick, as described in [2].

Table 1 Specification of fixed-point cells

Cell no.	Nominal purity of Cr (%)	Ingot mass (g)	Metal supplier
6SS-2	99.9	18.9	Kojundo Chemical Laboratories Co. Ltd.
6SS-3	99.99	18.8	Kojundo Chemical Laboratories Co. Ltd.
6SS-5	99.999	18.3	Leico

2.2 Furnace and Radiation Thermometer

Two effectively identical furnaces were used in the investigation, a Nagano M furnace (model VR20-A23) and a Nagano S furnace (Model VR20-A20). They were developed for high-temperature fixed-point realization, and have a carbon-fiberreinforced carbon-composite (C/C) single-heater element that indirectly heats the furnace tube, also of C/C-composite material, that holds the fixed-point cell. The furnaces are equipped with purge units that allow operation without a viewing window. Details of the furnaces are given in [6]. Due to the toxicity of chromium, a local extraction system was installed at the furnace view port.

The fixed-point plateaux were observed by an LP-3 radiation thermometer (manufactured by KE, Serial No. 80-40) with a nominal wavelength of 650 nm. The thermometer was not calibrated for the measurements, and therefore the uncertainty of the temperature values given in this paper is approximately 2 K.

3 Observed Plateaux

3.1 Dependence on Material Purity of the Peritectic and Eutectic Melting Plateaux

The plateaux were realized by a constant furnace-temperature setting offset, ΔT, relative to the fixed-point temperature. In the following, only melting plateaux are compared as the freezing plateaux regularly exhibited supercools showing the reluctance of the peritectic to begin freezing. In Fig. 1a, peritectic melting plateaux for the three cells are compared with the melt realized after freezing at $\Delta T = -20$ K and melted at $\Delta T = +20$ K. Although the melting range is already relatively small for cell 6SS-2 (99.9 % nominal purity), the plateau shape and the inflection-point temperature show a clear dependence on purity. Cell 6SS-5 (99.999 % nominal purity) shows a melting range of approximately 150 mK and a temperature 0.26 K higher than that of 6SS-2. The plateau duration is also seen to be different. This aspect is treated in Sect. 3.3.

In Fig. 1b, eutectic melting plateaux are shown. The dependence on purity is much more evident than for the peritectic melting plateaux.

3.2 Effect of Annealing on the Peritectic Melting Plateaux

The cells were kept for various time intervals at a temperature 20 K below the peritectic temperature prior to melting to investigate the effect of annealing. In Fig. 2, the peritectic melting plateaux of cell 6SS-3 are shown for annealing times of 0, 1, 2, 4, and 10 h. The melting range and the melting temperature are unchanged, but the duration of the plateau becomes longer as the annealing time increases. This is contrary to the M–C eutectics, for which the melting range becomes smaller and the temperature higher as the annealing time increases, while the plateau duration stays the same, although at a magnitude hardly noticeable except for the Fe–C eutectic [7].

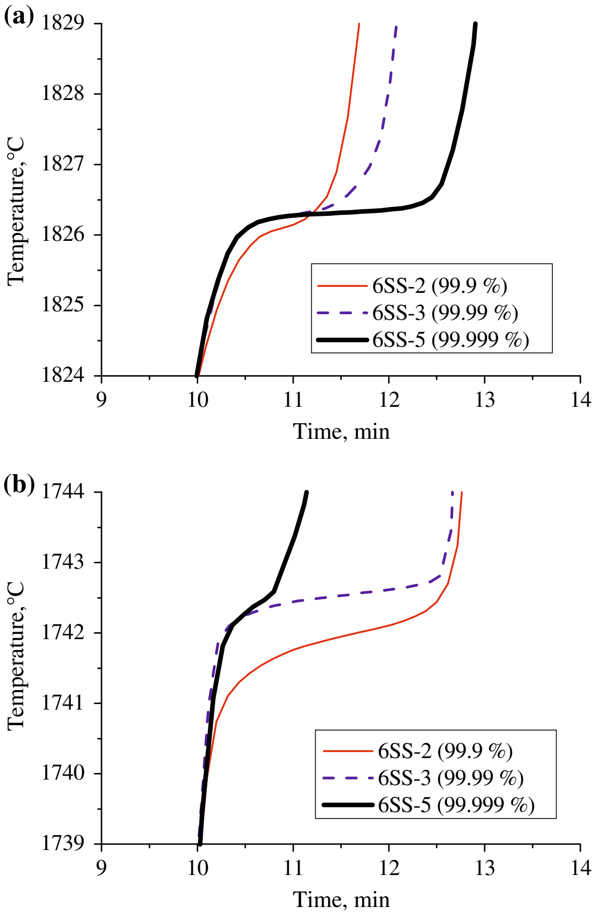
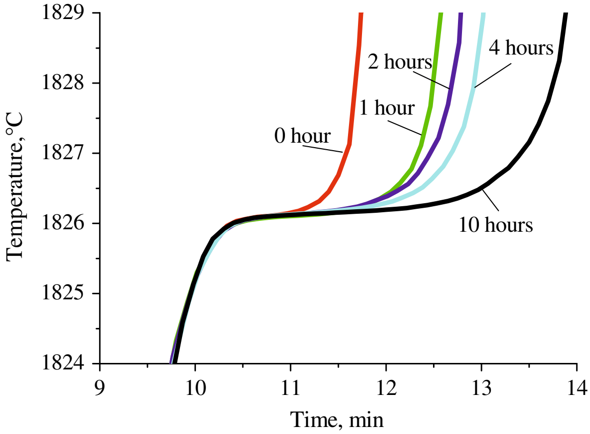


Fig. 1 Melting plateaux for cells made from metal powder of different purities: (**a**) Cr_3C_2–C peritectic point and (**b**) Cr_7C_3–Cr_3C_2 eutectic point

Fig. 2 Melting plateaux for cell 6SS-3 annealed 20 K below the peritectic point for various time intervals



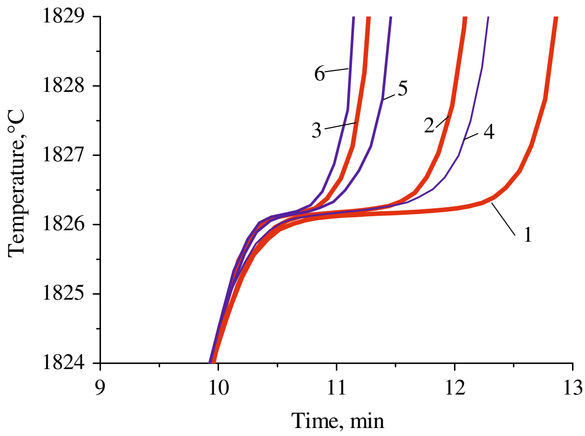


Fig. 3 Peritectic melting plateaux with cell 6SS-3 for repeated melt/freeze cycles. Plateaux are enumerated by the order of realization. Between plateau numbers 3 and 4, eutectic freezing and melting were realized

3.3 Reproducibility of Peritectic Melting Plateau Duration

The peritectic melting plateau duration was found to vary, even for a fixed annealing time. In Fig. 3, melting plateaux for cell 6SS-3 are shown when repeating the melt with $\Delta T = +20\,\mathrm{K}$ after the same freezing condition, $\Delta T = -20\,\mathrm{K}$, with no annealing. The plateau duration tends to become shorter with each successive melt. However, once the cell has been taken to a temperature low enough to realize the eutectic freezing point, the plateau length is seen to recover (plateau number 4).

To improve the reproducibility of the peritectic melting plateau duration, an intermediate step was introduced to the above procedure whereby the furnace temperature was kept at $\Delta T = -60\,\mathrm{K}$ for a period of 30 min, or at $\Delta T = -110\,\mathrm{K}$ for a period of 30 min, before the melt so that further "*freezing*" is imposed. The result is shown in Fig. 4, where three plateaux were realized after the $\Delta T = -60\,\mathrm{K}$ imposed

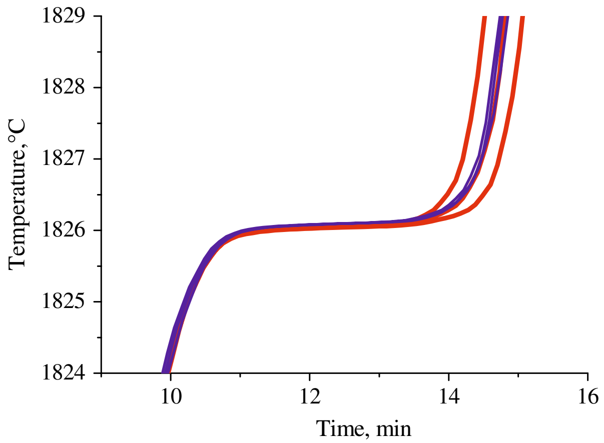


Fig. 4 Peritectic melting plateaux with cell 6SS-3 for repeated melt/freeze cycles with an imposed intermediate freezing step

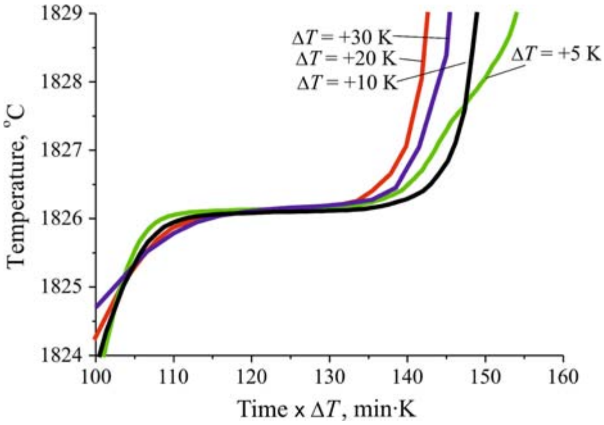


Fig. 5 Peritectic melting plateaux with cell 6SS-3 for various melting rates

freezing and three others after the $\Delta T = -110\,\mathrm{K}$ imposed freezing. With this additional "*freezing*," the plateau durations are virtually the same.

3.4 Dependence of the Peritectic Melting Plateaux on Melting Rate

After the imposed freezing (as described in Sect. 3.3), the furnace temperature setting offset ΔT during the melt was varied to test the effect of different melting rates. The result is shown in Fig. 5. The horizontal axis is taken to be the elapsed time multiplied by ΔT so that the plateau duration appears to be the same. No apparent dependence on the melting rate is seen near the inflection point within the repeatability of the plateaux. At the beginning and toward the end of the plateaux, furnace effects possibly influence the shape of the melting curve, a circumstance that is most apparent for melting with $\Delta T = +5\,\mathrm{K}$.

3.5 Dependence of the Peritectic Melting Plateaux on Rate of Preceding Freeze

In Fig. 6, melting plateaux of cell 6SS-2 (the least pure) are shown for melts with $\Delta T = +10\,\mathrm{K}$ with various rates for the preceding freeze, without the intermediate step of imposed freezing (described in Sect. 3.3). Out of eight plateaux realized, four of those of similar durations are plotted where the rate of the preceding freeze varied with the changing furnace-temperature setting offsets of $\Delta T = -5, -10, -15,$ and $-20\,\mathrm{K}$. No dependence of the plateau shape and temperature on the rate of the preceding freeze was detected within the repeatability of the plateaux.

3.6 Repeatability of the Peritectic and Eutectic Plateaux

The repeatability, evaluated as the standard deviation of the inflection point of the peritectic melting plateaux within a day, corresponding to Figs. 3–5 was 20, 18, and

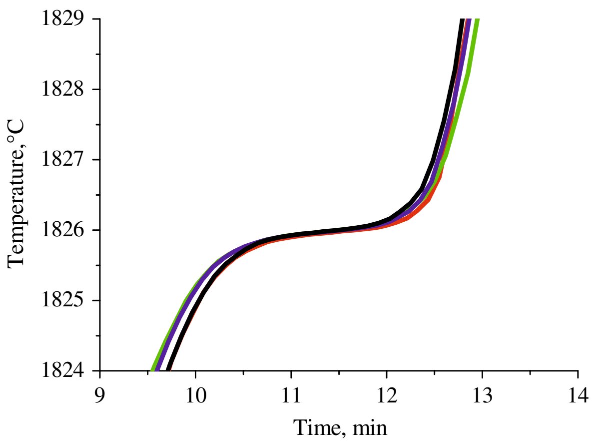


Fig. 6 Peritectic melting plateaux with cell 6SS-2 for various rates of the preceding freeze

21 mK, respectively. It was not possible to evaluate the repeatability of the freeze, due to the deep supercools.

On the other hand, the same (6SS-3) cell's eutectic melting plateau evaluation (graph not shown) resulted in a repeatability of 210 mK within a day.

3.7 Other Observations

On rare occasions, an alternative equilibrium temperature was observed at approximately 1,813°C, just below the peritectic point, in place of the peritectic plateau. A similar incidence has also been observed close to the eutectic point. The existence of meta-stable phase transitions is suspected.

4 Practical Issues

One concern for the practicality of the Cr_3C_2–C peritectic point is the health safety issue. Molten chromium was found to have a high vapor pressure and, together with the known toxic properties of certain Cr^{6+} compounds, we found it necessary to investigate whether the amount of vaporization poses a hazard to health.

The cell that was used most extensively in the current investigation, 6SS-3, was weighed before and after the investigation and the loss was found to be 0.74 g. The measurement extended over a 17-day period with an average of 8 h per day above 1,500°C. If we attribute all weight loss of the cell to chromium vaporization and calculate the chromium vapor density as the amount of vaporization per day divided by the inner volume of the lab room, we derive a value less than half of the American Conference of Governmental Industrial Hygienists (ACGIH) TLV-TWA allowed exposure level of $0.5\,\mathrm{mg}\cdot\mathrm{m}^{-3}$. Even so, we decided to take precautionary measures by installing a simple extraction system.

Another practical issue is the robustness of the cells. As described in [2], the C/C sheet inner insulation technique could not be employed for Cr_3C_2–C fixed-point cells. This means the breakage risk for these cells is potentially higher than for other materials. However, out of the seven cells fabricated so far, only one cell (6SS-5) showed metal leakage, but this was attributed to overfilling. No cells broke during the tests. The cell most extensively used, 6SS-3, experienced 138 melts (peritectic and eutectic) without failure. The reason for the apparent robustness may be attributed to the brittleness of the chromium carbides; the ingot has been seen to crack with the graphite crucible when a test cell was struck with a hammer.

5 Discussion

5.1 Effect of Impurities

As with any other fixed point, impurities were found to have a major effect on the fixed-point plateau. It is not yet clear why the impurity effect is more severe for the Cr_7C_3–Cr_3C_2 eutectic than for the Cr_3C_2–C peritectic point. One possible explanation is that impurities are rejected from the solid upon the peritectic freezing, and the eutectic freezing therefore starts with a larger impurity concentration in the remaining liquid. However, confirmation of this hypothesis awaits further investigation.

5.2 Effect of Annealing on the Peritectic Melting Plateau Duration

The effect of annealing has a totally different effect on the MC–C peritectics when compared to the M–C eutectics. However, the effect is of less concern since the temperature value is unaffected and only the duration varies.

The mechanism of this effect is different from the annealing effect for the M–C eutectics, which is explained by the variation in surface energy of the solid–liquid interface due to differences in eutectic structure size [7,8]. In [2], it is shown that the freezing of the peritectic involves a reaction between liquid and graphite to form a carbide that covers the graphite surface. Therefore, there is no apparent structure influencing the solid–liquid interface as in the case of eutectic freezing. The reaction continues by diffusion through the carbide layer once the graphite surface is covered. When the supply of graphite is infinite, as in the current case where the crucible is graphite, the freezing should continue until the liquid has totally solidified to form Cr_3C_2. However, the process will slow down significantly as the carbide layer thickens. The apparent termination of the freezing plateau is therefore not a true termination but an indication of this decreasing rate of solidification. The "annealing" that was performed in Sect. 3.2 is actually a continuation of the freeze. The elongation of the successive melting plateaux supports this interpretation.

The reason for the melting plateau becoming shorter on repeated melt/freeze cycles (Sect. 3.3) is not yet clear. The imposed freezing increases the peritectic carbide layer thickness, thereby recovering the plateau duration.

5.3 Repeatabilities of the Peritectic and Eutectic Melting Plateaux

We can only speculate on the reason why the peritectic melting plateau shows better repeatability than the eutectic melting plateau. Possible explanations for the inferior performance of the eutectic point are (1) sensitivity of the eutectic melting to impurities (cf. Sect. 5.1), (2) existence of meta-stable states near the eutectic melting temperature, (3) influence of the surface energy of the melt caused by complex eutectic structures, and (4) thermal effects due to imperfect enclosure of the cavity by the liquid–solid interface of the melting eutectic. This remains a subject of future studies.

6 Summary

The Cr_3C_2–C peritectic point has been investigated for its performance as a high-temperature fixed point. The observed repeatability of the melting plateau was around 20 mK, which is of a similar level as the best M–C eutectics evaluated to date. The evaluation of the freeze was obstructed by the regular occurrence of deep supercools. The second transition, the eutectic point of Cr_7C_3–Cr_3C_2, showed a repeatability of 210 mK and currently seems insufficient for primary standard use, though for industrial applications this level of repeatability at this temperature may be of interest. It should be noted that the above performance was achieved with a conventional filling without the C/C-sheet wick. It is of interest to see whether or not any improvement can be obtained by applying the improved filling method with the C/C-sheet wick.

As with any fixed point, the Cr_3C_2–C peritectic point was shown to be strongly influenced by impurities, though less strongly than the eutectic plateau. Thermal history affected the plateau duration only; the fixed-point temperature remained the same. The rate of melting showed no apparent influence on the plateau inflection-point temperature.

Health concerns related to Cr^{6+} were allayed. The robustness of the cell so far is not an issue. Studies on the effect of impurities and the evaluation of long-term stability are envisaged in the future.

Together with the WC–C peritectic point, which also shows promise [3], the MC–C peritectic points are proving to be a low-cost alternative to M(C)–C eutectic points, though with increased complications of operation.

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