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SHORT COMMUNICATION

Metal carbide-carbon peritectic systems as high-temperature fixed points in thermometry

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Abstract

WC–C, Cr₃C₂–C and Mn₇C₃–C peritectic systems were investigated for their potential of serving as high-temperature reference points in thermometry. Mixtures of high-purity graphite powder with W, Cr and Mn powder of 99.99%, 99.9% and 99.95% purity by mass, respectively, were placed in graphite blackbody crucibles and melting/freezing plateaus were observed by means of a radiation thermometer. The observed melting temperatures were 2749 °C (WC–C), 1826 °C (Cr₃C₂–C) and 1331 °C (Mn₇C₃–C), with a repeatability—in each case—of 0.02 K. The melting range for WC–C and Cr₃C₂–C peritectics was roughly 0.1 K. WC–C showed a flat freezing plateau that agreed with the melting plateau within the repeatability. The three fixed points are possible candidates, like the metal (carbide)–carbon eutectic fixed points, in the realization of an improved high-temperature scale above the copper point.

1. Introduction

Liquid–solid phase transformations in binary metal–carbon alloys equilibrating the three phases of liquid, the solid metal (or metal carbide) phase and solid carbon (graphite) have been successfully applied to metal (or metal carbide)–carbon (M(C)–C) *eutectic* fixed points [1]. These fixed points are currently the target of a joint effort among national metrology institutes aimed at establishing internationally recognized reference temperatures for a temperature scale above the copper point (1084.62 °C) up to 3200 °C [2].

Besides the *eutectic* reaction, there is another reaction involving equilibrium among the same three phases: the *peritectic* reaction [3]. Whereas the M(C)–C *eutectic* reaction involves melting of a two-phase solid consisting of the metal (carbide) phase and graphite into a single-phase liquid, the metal carbide–carbon (MC–C) *peritectic* reaction involves melting of a single phase of metal carbide into a two-phase mixture of liquid and solid graphite.

The importance of M(C)–C *eutectics* arises from the fact that they can be realized in graphite crucibles, which allow

high emissivity and robustness. As long as the graphite of the crucible is sufficiently purified, it does not contaminate the fixed-point metal, since carbon is already a component in the phase equilibrium. The same advantage can be expected for MC–C *peritectics*.

This paper reports the result of a preliminary investigation on the applicability of MC–C *peritectic* systems as high-temperature fixed points above the copper point.

2. MC–C peritectic fixed points

Binary phase diagrams are shown for the W–C, Cr–C and Mn–C systems in figure 1. The W–C system, for instance, has several carbide phases, the one closest to the graphite (C) phase being the WC phase. No other phases exist in between the WC and C phases, so WC should be stable in graphite crucibles up to 2776 °C, above which the phase can no longer exist. At this temperature, the peritectic temperature, the WC phase is in equilibrium with the liquid phase and graphite (marked by ‘A’ in the diagram). Here, one can expect to

observe an arrest in temperature accounting for the latent heat that manifests itself as a flat plateau upon melting. The molten liquid solution is lower in carbon content than the carbide. When this solution is cooled, it will react with the graphite from the precipitated solid or from the crucible and WC is formed at the peritectic temperature. Whereas in the M(C)–C eutectic reaction the eutectic temperature is the *lowest* temperature at which the *single liquid phase* can exist, in the peritectic reaction the peritectic temperature is the *highest* temperature at which the *single solid carbide phase* can exist.

Similarly, for the Cr–C system (shown in figure 1(b)), the Cr_3C_2 –C peritectic point ('A') should be realizable. For the Mn–C system (shown in figure 1(c)), the peritectic reaction between the Mn_7C_3 phase on the one hand and the liquid and graphite phases on the other ('A') should be observed.

These three MC–C peritectic points (WC–C: 2776 °C, Cr_3C_2 –C: 1811 °C, Mn_7C_3 –C: 1333 °C) are of interest because they are all located above the freezing point of copper (1084.62 °C), the highest defining fixed point in the International Temperature Scale of 1990 (ITS-90); moreover they are all contained within the temperature range covered by the M(C)–C eutectic points. The MC–C peritectic points are listed on the left side of figure 2 along with the M(C)–C eutectic points on the right side of the same figure. (The temperature values for the new fixed points on the left are taken from [4].)

In figure 1(a) one notices that a eutectic point exists just below the peritectic point (marked by 'B' in the diagram). This is the eutectic including—apart from the liquid phase—the two solid carbide phases WC and WC_{1-x} . If there is still liquid solution present when the peritectic freezing is completed, then it will remain in the liquid state down to this eutectic temperature, where a second plateau should be observed. For the Cr–C system the second plateau would occur at the eutectic point including the phases Cr_7C_3 and Cr_3C_2 ('B'). In the case of Mn–C there is no eutectic reaction between any of the carbide phases, but instead a second peritectic reaction between the ϵ (Mn carbide) phase and the liquid + Mn_7C_3 phase is seen (marked by 'C').

3. Preparation of the fixed-point cells

To investigate the suitability of the phase transformations observed at these points as thermometric references, one blackbody cell was fabricated for each of the three fixed-point materials and the plateaus were observed.

Four furnaces were employed in this investigation for the cell preparation and the plateau observation: a vertical furnace (manufactured by Nagano, model VR20-A10) [5], two essentially identical horizontal furnaces (manufactured by Nagano, models VR20-A20, -A23) [6] and another horizontal furnace with a maximum operating temperature of 3500 K (manufactured by VEGA International, model BB3500YY) [7].

The crucible design is the same as the one described in [8] with an outer dimension of 24 mm and incorporates a blackbody cavity of estimated effective emissivity 0.9996. In the current investigation, neither inner sleeve nor inner insulation material such as employed in some of the eutectic fixed points [7] was used. The graphite crucible was purified before and after machining to less than 5×10^{-6} ash content.

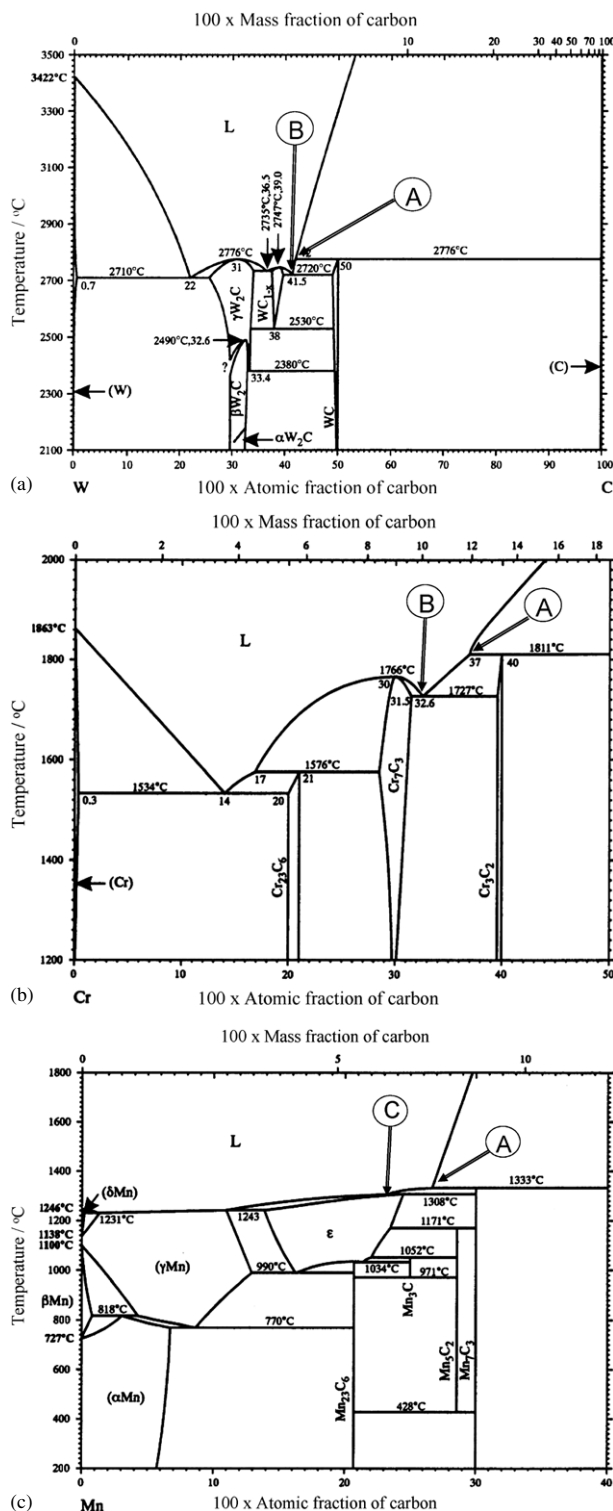


Figure 1. Binary alloy phase diagrams (original diagrams from [4]): (a) tungsten–carbon, (b) chromium–carbon and (c) manganese–carbon. A: MC–C peritectic point, B: MC–MC eutectic point, C: MC–MC peritectic point.

No baking of the crucible was done before filling. High purity graphite powder of 99.9999% (supplier Alpha Aesar) was used in the powder mixture for filling.

The fixed point cells were fabricated in the following manner. For the Cr_3C_2 –C peritectic, Cr powder of 99.9%

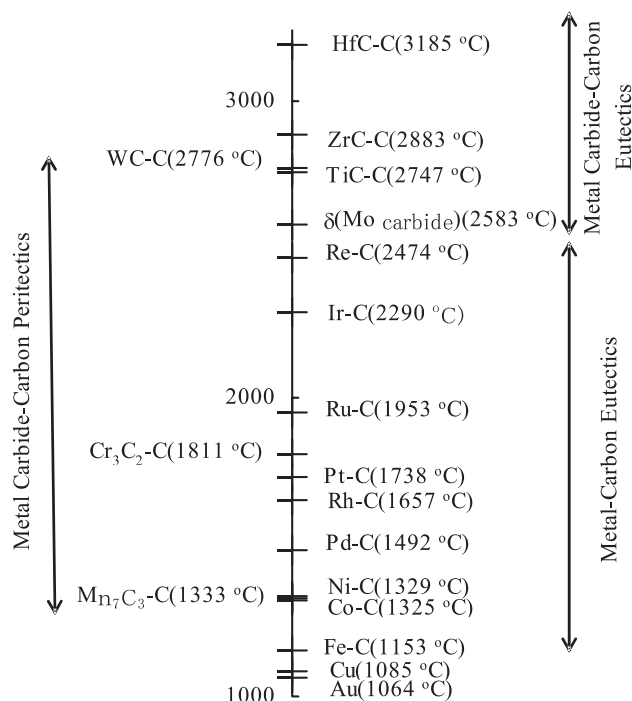


Figure 2. High-temperature fixed points of metal-carbon systems.

purity (supplier Kojundo Chemical Laboratories Co., Ltd) was mixed with the graphite powder at the carbide composition of 40% atomic fraction of carbon. The crucible was placed in a vertical furnace, which was then evacuated and flushed with argon. Subsequently the furnace was raised to above the Cr₇C₃-Cr₃C₂ eutectic point of around 1727 °C in vacuum and brought down to room temperature for inspection. The ingot appeared to be in a sintered state. The cell was placed back in the furnace and was raised this time to above the peritectic melting temperature. After cooling to room temperature, the ingot still appeared to maintain the same sintered porous state without flowing. This is similar to what has been observed for hyper-eutectic ingots [7, 9]. Finally the graphite crucible cap was mounted and the cell was placed in the Nagano horizontal furnace for plateau observation.

For peritectic WC-C, W powder of 99.99% purity (supplier Kojundo Chemical Laboratories Co., Ltd) was mixed with graphite powder at the carbide composition of 50% atomic fraction of carbon. The graphite crucible was packed with the mixture, the crucible cap closed and the cell was then placed in the horizontal high-temperature furnace BB3500YY, which was raised once to above the WC_{1-x}-WC eutectic point (2720 °C) and cooled with the expectation that a sintered state was thus formed, and then was taken to a higher temperature for plateau observation.

For the Mn₇C₃-C peritectic, Mn powder of 99.95% purity (supplier Leico Industries, Inc.) was mixed with graphite powder at 37% atomic fraction of carbon. The mixture was made richer in graphite than the carbide composition of 30%, after an initial attempt at the carbide composition failed to produce a porous sintered state. The cell was then closed and placed in the Nagano horizontal furnace for plateau observation. When approaching the temperature around the

melting of the ε(Mn carbide) phase (1308 °C), a sudden generation of heat was observed, causing the cell temperature to rise by a few hundred degrees, thereby surpassing the melting temperature of the peritectic for a few seconds.

The WC-C, Cr₃C₂-C and Mn₇C₃-C cells, thus prepared, contained 32.6 g, 11.3 g and 15.3 g of the metal carbon mixture, respectively.

4. Plateau observations

The melting/freezing plateaus were observed by means of an LP-3 radiation thermometer (manufactured by KE Technologie) at a wavelength of 650 nm. The furnaces were operated under Ar flow with the front window removed to allow unobstructed sighting of the blackbody cavity. For WC-C and Cr₃C₂-C several melting/freezing plateaus for the eutectic points (WC_{1-x}-WC, Cr₇C₃-Cr₃C₂) were realized prior to peritectic melting and freezing. After the very first melting/freezing plateaus, induced to tune the furnace temperature setting, three melting/freezing cycles were realized for determining the melting and freezing temperatures by varying the furnace temperature starting from temperatures about 10 K to 30 K below to temperatures about 10 K to 30 K above the peritectic phase transition temperature. Finally, another melt was realized for the eutectic transformation. For Mn₇C₃-C only the observation of the peritectic melt/freeze was attempted.

Examples of the observed melting/freezing plateaus for the three MC-C peritectics are shown in figure 3. The melting temperature (T_{melt}), its uncertainty U , the repeatabilities of T_{melt} and the freezing temperature (T_{freeze}) and the melting/freezing temperature difference are shown in table 1. T_{melt} was identified with the inflection point of the melting curve, similarly to what is commonly practised in the case of M-C eutectics. The maximum freezing temperature after recalescence was taken as T_{freeze} . The uncertainty U includes the uncertainty in scale realization and the measurement uncertainty. The latter consists of the instability of the radiation thermometer, size-of-source effect, the correction for the blackbody emissivity and the repeatability of the plateaus.

The melting temperatures for the WC_{1-x}-WC and the Cr₇C₃-Cr₃C₂ eutectic transformations were 2720 °C and 1742 °C, respectively. The observed melting plateaus had much poorer characteristics than their peritectic counterparts: duration of about 1 min, melting ranges of roughly 0.5 K to 1 K and repeatability of a few hundred millikelvin. The eutectic melting plateaus observed before and after the peritectic transformations were quite similar in shape and duration. For the eutectic freezes, no freezing temperature was defined due to extremely deep supercooling. No clear plateau could be observed for ε(Mn carbide)-Mn₇C₃ peritectic melting, although a sharp recalescence from a deep supercooling was observed around 1250 °C, indicating the existence of a liquid phase after peritectic freezing.

5. Discussion

The melting ranges observed for the WC-C and Cr₃C₂-C peritectics are roughly 0.1 K, and the repeatability of the melting points for all three peritectic fixed points was 0.02 K.

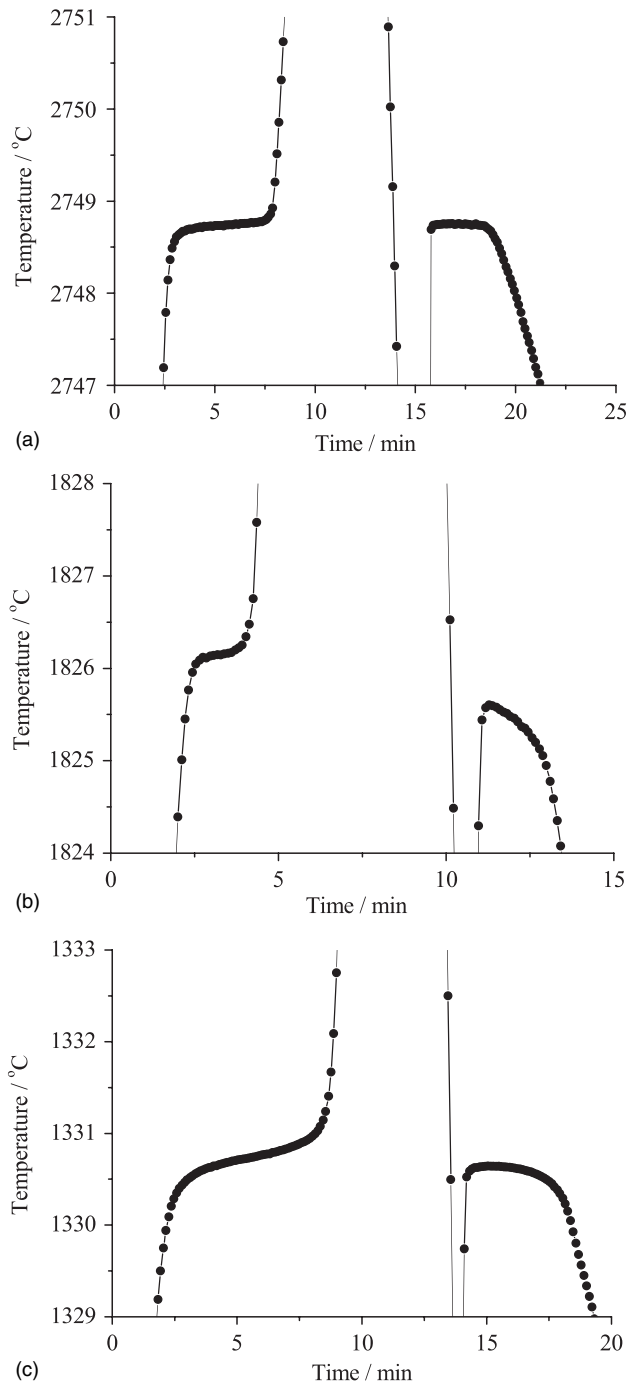


Figure 3. Peritectic melting and freezing plateaus. (a) WC–C, (b) Cr₃C₂–C and (c) Mn₇C₃–C.

This is all surprisingly small if one considers the fact that the nominal purities of the metal powders in the cells were 99.99%, 99.9% and 99.95% for WC–C, Cr₃C₂–C and Mn₇C₃–C, respectively. For M–C eutectic fixed points plateaus of similar quality could only have been achieved with 99.999% pure material, i.e. with the purest metals available thus far.

To the authors' knowledge, there has been no prior investigation of peritectic transitions applied to thermometric fixed points. Study of peritectic solidification predicts the formation of a wide variety of different dendritic, cellular or planar microstructures depending on the growth velocity and

temperature gradient at the freezing front [10]. Therefore, it is surprising to find the extremely flat and reproducible melting plateaus as seen for WC–C and Cr₃C₂–C and the flat freezing plateaus for WC–C and Mn₇C₃–C.

The observation of eutectic melts and freezes indicates that there is still liquid solution existing after peritectic solidification; this would presuppose either the system being in a hypo-peritectic state—which can be excluded here since graphite exists in abundance as the crucible material—or the peritectic reaction being left incomplete—due to its sluggishness—with continuing extraction of heat involving the cooling down of the ingot. In eutectic solidification diffusion processes towards equilibrium take place largely by diffusion through the liquid whereas in the peritectic transformation diffusion must take place through the solid phase [11], an inherently slower process.

Although this needs to be confirmed, it can be assumed from this that the carbide phase as it is formed covers the surface of the graphite which is present, thus inhibiting further reaction of the liquid with the graphite within the time scale of the solidification process. This phenomenon is referred to as 'envelopment', occurring in the case of non-equilibrium solidification of peritectic systems [11].

The existence of the eutectic plateau is interesting from the point of view that apparently two fixed-point temperatures can be realized by a single cell, in principle enabling a scale realization by two-point fitting [12, 13]. However, from a practical point of view the two temperatures are too close and the quality of the eutectic plateau too poor for high-accuracy scale realization in this way.

Although still at a preliminary stage of investigation, the potential advantages of the MC–C peritectic fixed points over the M(C)–C eutectic fixed points should be noted. The observed WC–C peritectic point (2749 °C) coincides with the TiC–C eutectic point (2747 °C). One difficulty encountered for TiC–C is the unavailability of high-purity Ti powder; on the other hand high-purity W powder is easily obtained. The peritectic temperature of Cr₃C₂–C (1826 °C) is close to the Pt–C eutectic point (1738 °C), the latter incorporating one of the most expensive noble metals. The Mn₇C₃–C peritectic point (1331 °C) can replace the Co–C and the Ni–C eutectic points (1324 °C and 1329 °C) if the plateau can eventually be shown to be of better quality with the availability of high-purity Mn.

6. Conclusions

MC–C peritectic phase transitions were investigated for WC–C, Cr₃C₂–C and Mn₇C₃–C, and their potential as high-temperature fixed points similar to M(C)–C eutectic fixed points was confirmed, although at a preliminary stage.

Other carbides that have a peritectic transition equilibrating with graphite are α -SiC (2830 °C), Al₄C₃ (2173 °C) and β -PuC₂ (~2400 °C). (The temperature values are from [14] for α -SiC and from [4] for the other two.) However, an attempt to realize the α -SiC–C peritectic transition resulted in heavy deposition of the material on the furnace interior, blocking its viewing by the radiation thermometer. This is understandable if one considers the large temperature difference between the peritectic point and the melting point of pure Si. No attempt

Table 1. Characteristic data for peritectic melting and freezing.

Type	$T_{\text{melt}}/^{\circ}\text{C}$	$U(k = 2)/\text{K}$	Repeatability (σ) / K		
			For T_{melt}	For T_{freeze}	$(T_{\text{melt}} - T_{\text{freeze}})/\text{K}$
WC–C	2748.91	2.0	0.02	0.05	–0.02
Cr ₃ C ₂ –C	1826.15	0.8	0.02	0.26 ^a	0.74 ^a
Mn ₇ C ₃ –C	1330.72	0.4	0.02	0.02	0.09

^a Only two measurement data available for the freeze, due to deep supercooling.

has been made to realize the Al₄C₃ yet, since the phase diagram for the Al–C system resembles that for Si–C.

Further investigations of the MC–C peritectic phase transitions are envisaged at NMIJ to ascertain the reproducibility between different cells, and to evaluate the dependence on impurity, dependence on (pre)freezing rate, long-term stability as well as sensitivity to the filling method.

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