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Laser melting of uranium carbides

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ABSTRACT

In the context of the material research aimed at supporting the development of nuclear plants of the fourth Generation, renewed interest has recently arisen in carbide fuels. A profound understanding of the behaviour of nuclear materials in extreme conditions is of prime importance for the analysis of the operation limits of nuclear fuels, and prediction of possible nuclear reactor accidents. In this context, the main goal of the present paper is to demonstrate the feasibility of laser induced melting experiments on stoichiometric uranium carbides; UC, $UC_{1.5}$ and UC_2. Measurements were performed, at temperatures around 3000 K, under a few bars of inert gas in order to minimise vaporisation and oxidation effects, which may occur at these temperatures. Moreover, a recently developed investigation method has been employed, based on *in situ* analysis of the sample surface reflectivity evolution during melting. Current results, 2781 K for the melting point of UC, 2665 K for the solidus and 2681 K for the liquidus of U_2C_3, 2754 K for the solidus and 2770 K for the liquidus of UC_2, are in fair agreement with early publications where the melting behaviour of uranium carbides was investigated by traditional furnace melting methods. Further information has been obtained in the current research about the non-congruent (solidus–liquidus) melting of certain carbides, which suggest that a solidus–liquidus scheme is followed by higher ratio carbides, possibly even for UC_2.

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1. Introduction

Uranium–plutonium carbides are one of the candidate fuels for Generation IV nuclear plant systems, and particularly for the gas-cooled fast reactor (GFR) and the very high temperature reactor (VHTR) [1]. These fuel materials have a high fissile metal density and are able to withstand very high temperatures, during normal and accidental reactor operations. The operational temperature of the GFR and VHTR is between 1300 and 1500 K and under accidental conditions up to the melting point of the fuel. The carbides and nitrides often seem to be the best compromise for these reactors, due to their high melting point (compared with (Pu,U) alloys), high density of heavy metals and good conductivity (compared with the oxide fuels). Although the nitrides have a higher heavy metal density than the carbides, producing a fuel pellet of sufficient density (99% or more of the theoretical density) is difficult, and therefore the carbides would be the preferred fuel material. In particular for the GFR, a likely fuel material is a mixed (Pu,U)C kernel, surrounded by an inert layer of SiC [2]. Although these carbides were previously studied as potential fuels, further research is now required, due to the high operating temperature of the GFR, and to establish any interactions between the fuel kernel and the surrounding layers, and the formation of solid, liquid and/or gaseous phases [3,4]. In this context, within a more general assessment of the ternary system U–Si–C, the present paper introduces the laser induced melting of uranium carbides (UC, $UC_{1.5}$ (U_2C_3) and UC_2), and the measurement of high temperature phase transitions.

Fig. 1 shows the uranium–carbon phase diagram calculated using Thermocalc® and the thermodynamic database, FUELBASE, developed by Guéneau et al. [2], which is based on the current literature. Three stoichiometric phases exist; UC, $UC_{1.5}$ and UC_2. UC is stable from room temperature up to 2799 K where it melts congruently. $UC_{1.5}$ (U_2C_3) is stable from room temperature to approximately 2089 K, where it decomposes to form UC and UC_2. UC_2 is stable at high temperatures, and forms above 1743 K, and it probably melts congruently at 2700 K. Two polymorphs of UC_2 exist [5]; the high temperature cubic form and the low temperature tetragonal form, with the transformation occurring at approximately 2044 K. Below the melting temperature it is proposed that a solid solution exists between UC and UC_2, with a miscibility gap between 2089 and 2325 K. The solidus–liquidus between UC and UC_2 has two maxima at 2799 K (the melting point of UC) and 2709 K (near UC_2), and a minimum at approximately 2686 K (near $UC_{1.6}$).

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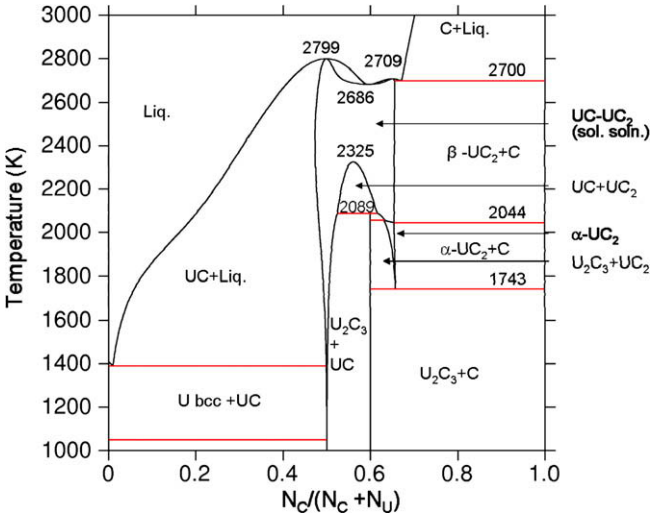

Fig. 1. Calculated U-C phase diagram using Thermocalc® and the thermodynamic database FUELBASE [4] (N_C = moles of C; N_U = moles of U).

Although the calculated phase diagram shows definitive values for the melting points of UC, UC_2 and the solidus–liquidus line, experimental data in the literature show significant scatter. The melting point of UC and UC_2 are respectively reported to be between 2553 [6] and 2973 K [7] and between 2713 [8] and 2803 K [9]. Table 1 shows the melting point temperature reported in the literature.

Variation in experimental values may arise, for example, from oxygen or nitrogen contamination [13,5], or volatilisation during melting [8].

Previous measurements of the solidus and liquidus were made using traditional furnace heating methods. Mallett et al. [10] measured solidus and liquidus temperatures of samples between UC and UC_2 prepared using argon arc melting. A sample with a ridge or peak was placed on a graphite ring and heated under vacuum in a furnace. The temperature at which the ridge or peak rounded was recorded as the solidus, and the temperature at which the sample lost shape and fell through the ring, as the liquidus. Benz et al. [8] determined the solidus by inductively melting samples. The samples were prepared by cold pressing and sintering different ratios of pre-prepared uranium carbides under vacuum, to form a cylindrical shape, in to which a small hole was made in the top surface. The sample was slowly heated using an induction furnace under a helium atmosphere until liquid was observed in the hole. At this point the temperature for the solidus was recorded, using an optical pyrometer focused on the hole. After heating, the uranium content was reanalysed to account for any change in composition due to volatilisation.

In the current laser induced melting experiments, very high temperatures ($T > 3000$ K) are obtained in short (10^{-2} s) pulses to melt the sample surface. The sample temperature is recorded by a fast pyrometer, and inflections in the recorded thermograms reveal phase transitions. A second independent method for measuring phase transitions, called the Reflected Light Signal method (subsequently described), is also used.

The advantages to using laser melting, over traditional methods, are four-fold.

(1) The problem of volatilisation and/or contamination (i.e. oxidation) during testing is minimised, as the test lasts between 20 and 50 ms. Experiments may also be completed under high inert gas pressures, further inhibiting volatilisation.
(2) The samples are tested in effectively container-less conditions, through only surface melting, and as only a small area of the sample surface is melted, tests may be easily and quickly repeated.
(3) As only the surface of the sample is melted during testing, the material behaviour can be observed both during heating through melting and during cooling after freezing, which is not the case with, for example, Benz et al's experiments [8], where the sample is destroyed upon melting.
(4) Reflected Light Signal method for determining phase transitions provides an independent, repeatable test to establish the onset of melting, freezing and other phase transitions. Liquidus and solidus measurements may therefore be performed during one experiment, using a single sample, by analysing the Reflected Light Signal and thermogram.

Laser induced melting combined with the Reflected Light Signal method, is an altogether novel method, different from all the previous techniques employed to investigate the high temperature properties of nuclear materials. Comparison between results from this study and earlier results will therefore lead to a deeper and more comprehensive understanding of the behaviour of the U-C system at high temperatures.

2. Experimental

2.1. Sample preparation

Samples were prepared using argon arc melting of uranium metal and graphite splinters in the correct ratios, and were subsequently analysed using XRD. Samples were re-melted several times to produce an homogenous product, which was then cut, using a diamond saw, to produce 'quasi' disk-shaped specimens with two flat surfaces. Samples were stored under vacuum to minimise oxygen and nitrogen contamination. Samples were mounted in an alumina or graphite ring, sometimes fixed using a high temperature resistant ceramic glue (Cotronics©).

2.2. Experimental set up

A 4.5 kW Nd:YAG cw programmable laser was used in short pulses (a few ms) to melt a circular spot of approximately 2–3 mm in diameter on the surface of a uranium carbide sample. Samples were shot under low argon pressure (up to 0.2 MPa).

The sample temperature was detected by means of a fast pyrometer (operating close to 650 nm), calibrated against standard lamps with an uncertainty of approximately ±0.3% at 2500 K. A

Table 1
Reported value of UC and UC_2 melting point, T_m.

Carbide	T_m (K)							
UC	2763 ± 40	2553 ± 50	2973	2663	2683	2768 ± 30	2863	–
	2798	–	–	–	2833	2798	–	–
	2833 ± 50	–	–	–	–	2788	–	–
UC_2	2753	–	–	–	2803	2753	–	2713 ± 40
Ref.	[5]	[6]	[7]	[10]	[9]	[11]	[12]	[8]

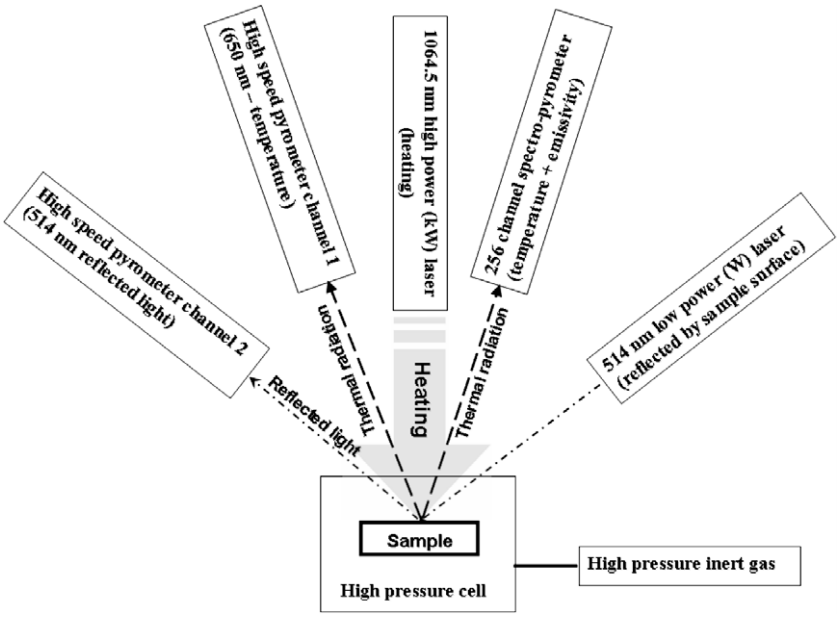

Fig. 2. Block synopsis of the experimental set up used in this work for the laser annealing and melting of uranium carbides.

total uncertainty band of ±0.7% at 3000 K was conservatively estimated for the measured temperature to take into account uncertainty in the sample emissivity and other experimental parameters. The accuracy of measured brightness temperature was checked to be better that 0.5% of the recommended value for the melting point of Mo (2530 K) [14].

Two methods [14] were used for the detection of melting and other phase transitions. The first method consists of conventional thermal analysis of pulse-heating thermograms where events, which are accompanied by latent heat exchanges, are apparent as plateaux or inflection points in the curve, $T = T(t)$, where t is time.

The second method, the Reflected Light Signal method, involves detection of the variations in the reflectivity of the sample surface, which often accompanies the formation of a new phase. This analysis was performed by means of a 1 W, 514 nm Ar^+ laser beam, which was reflected by the sample surface and then detected by a two-channel pyrometer. A suitable combination of the two methods (see the block synopsis in Fig. 2) permits a consistent understanding of the phenomena involved in the whole process of heating, melting, solidification and cooling.

3. Results

3.1. Phase analysis

Of the three samples prepared using argon arc melting, UC and UC_2 were phase pure, except for trace amounts of other impurities (mostly uranium oxides). In contrast, $UC_{1.5}$ was a full mixture of UC and UC_2, and also showed trace amounts of UO_2. Although U_2C_3 is the thermodynamically stable phase at ambient temperature for the composition $UC_{1.5}$, it does not readily form on rapid cooling, such as experienced during arc melting, and annealing is required for the phase to form [5].

3.2. Laser melting

3.2.1. General observations

The solidus and/or liquidus were measured for the U-C compounds, UC, $UC_{1.5}$ and UC_2. Samples were shot under low Ar pressure, and were robust and able to withstand numerous laser shots. After melting a small (2–3 mm diameter) solidified molten pool could be observed. In some circumstances, a black ring surrounding the pool was seen, which may be due to oxidation during testing. Little volatilisation of the samples was observed. Preliminary tests were performed, in order to ensure the uranium carbides could be fast heated above the melting point, without burning the sample (uranium carbides are known to be highly pyrophoric in the presence of even low traces of oxygen [5]).

3.2.2. UC

Fig. 3 shows thermograms obtained during the melting of UC, which were generated using two different laser heating profiles, one high and fast (maximum power of 1250 W over 20 ms), the other lower but longer (maximum power of 750 W over 30 ms). In both cases the samples were heated well above the reported melting temperature for UC, to 3500 K using pulse 1 and to 3179 K using pulse 2. On cooling excellent thermal arrests were observed at 2776 and 2778 K for pulses 1 and 2, respectively. The noise observed at the maximum of thermogram 1 is believed to be boiling on the sample surface. By reducing the maximum

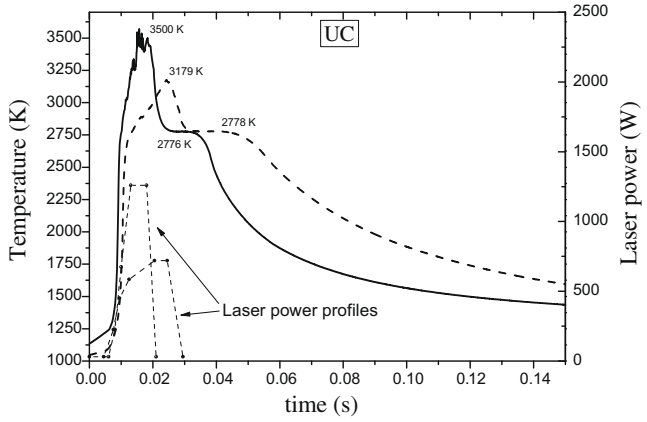

Fig. 3. Thermograms for two UC laser melting tests, heated using different laser heating profiles pulse 1 (solid) and pulse 2 (dashed).

temperature, the interference was removed, as shown by thermogram 2. The curves obtained do not show further inflections during heating or cooling, indicating that UC melts congruently and undergoes no phase changes below the melting temperature. Fig. 4 shows a micrograph of the sample after laser melting, and the uniform solidified molten pool formed.

3.2.3. $UC_{1.5}$

Fig. 5 shows the curves obtained during melting of $UC_{1.5}$. If a distinct liquidus and solidus exist, they are close and phase transitions during heating and melting complex. The Reflected Light Signal method was also used, to distinguish phase transitions. A high and long laser heating profile was applied (1 kW, 40 ms). The maximum temperature reached (3300 K) was well over the reported melting temperature at $UC_{1.5}$. On heating, an inflection occurred around 2665 K, which may be attributed to the onset of melting (i.e. solidus). The inflection also corresponds well to the start of large vibrations in the Reflected Light Signal. On cooling an excellent thermal arrest was observed at 2672 K (i.e. liquidus), which again agrees well to the end of the vibrations in the Reflected Light Signal.

Fig. 6 shows a micrograph of the $UC_{1.5}$ solidified molten pool after melting, which does not exhibit the same uniform features of the UC pool (i.e., an hour-glass feature, ripples and cracks). Within the experimental uncertainty, the solidus and liquidus appear close at $UC_{1.5}$, suggesting this composition is near to congruent melting. However, both the measured thermograms (Fig. 5) and the molten surface morphology (Fig. 6) are more complex than for UC, and therefore it is still to be demonstrated, whether the eutectic composition is stoichiometric $UC_{1.5}$ or a composition in its vicinity. The presence of two phases in this sample (UC and UC_2), and the possible formation of U_2C_3, may further complicate the melting and cooling processes.

On cooling, a further inflection is observed in the thermogram at approximately 2032 K, which may correspond to a solid–solid phase transition (2038 K), to be studied in better detail.

3.2.4. UC_2

In contrast to the previous thermograms, that for UC_2 (Fig. 7) does not exhibit a significant freezing plateau. The Reflected Light Signal and its derivative were relied upon to obtain the transition temperatures. On heating, the derivative of the Reflected Light

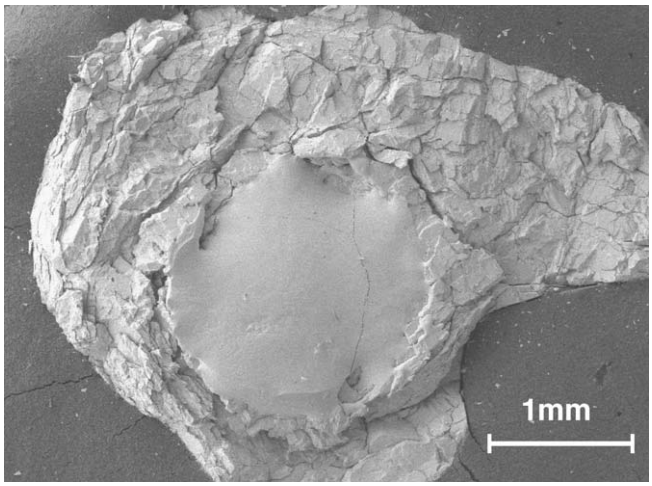

Fig. 4. SEM of UC sample (pale grey region) after laser induced melting showing uniform molten pool of approximately 2 mm diameter. The sample is set in the high temperature resistant ceramic glue (dark grey region).

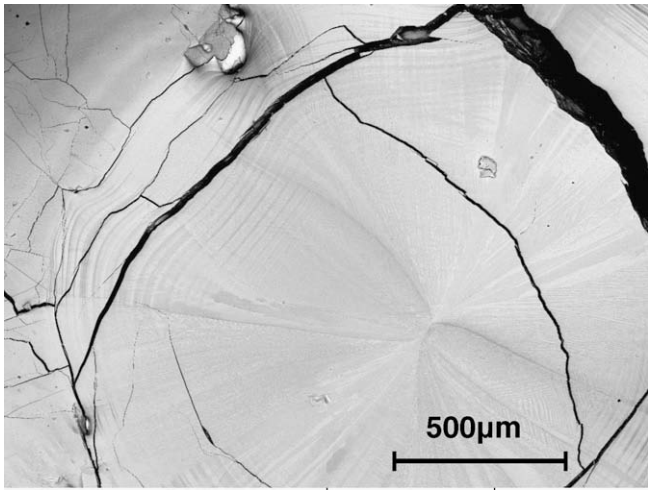

Fig. 6. Image of the surface of the solidified molten pool for the composition $UC_{1.5}$. Ripples and cracks in the surface, and the 'hour-glass' feature suggest complex melting.

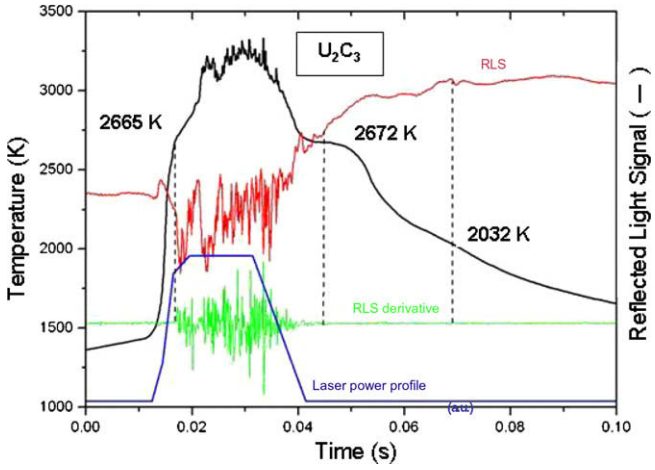

Fig. 5. $UC_{1.5}$: Thermogram, laser heating profile, Reflected Light Signal, and derivative of the Reflected Light Signal.

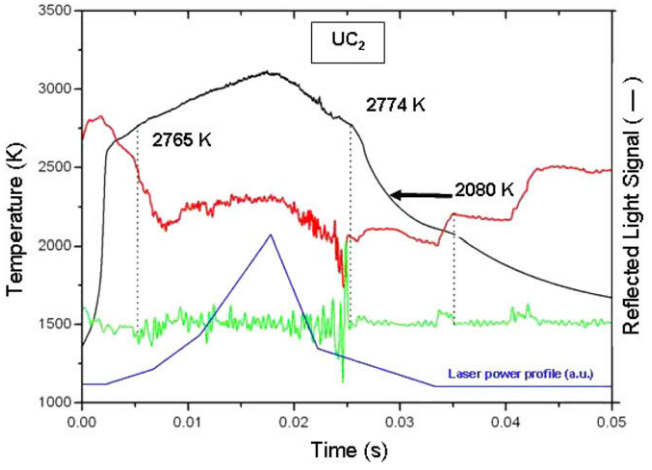

Fig. 7. UC_2: Thermogram, laser heating profile, Reflected Light Signal, and derivative of the Reflected Light Signal.

Signal showed significant vibrations after 2765 K, suggesting the formation of liquid at the surface above this temperature. On cooling an inflection was observed at 2774 K, however with no significant plateau. The inflection is associated with a large change in the vibrations in the Reflected Light Signal, suggesting solidification. As in the case of $UC_{1.5}$, the reported behaviour suggests that the UC_2 liquidus and solidus are close, but also that the melting/freezing process is complex. A more extended study, including investigation of melting in non-stoichiometric compositions around UC_2, will complete the analysis of this phase diagram region.

A further inflection is again seen during cooling, at 2080 K, and a marked change in the Reflected Light Signal, larger than that observed in $UC_{1.5}$, is noted. The inflection may be attributed to the α-UC_2 to β-UC_2 transition.

4. Discussion

Table 2 shows a comparison between the solidus and liquidus values obtained. Of the three compositions, UC has the best reproducibility, which is most likely because of its single phase and congruent melting. $UC_{1.5}$ and UC_2 also show good reproducibility, but identification of the solidus and liquidus is more challenging, because of the less well defined thermograms obtained.

Little data exists on the optical properties of the uranium carbides. The emissivity for UC is given as 0.5 [15] and, in the absence of other data, was used for all uranium carbide compositions tested to calculate the 'real' temperature recorded by the optical pyrometer. Bober et al. [16], actually observed that UC emissivity varies across the melting point from about 0.55–0.45. However, in the current experiments, only a small inflection in the $T(t)$ curve was normally observed upon melting (Figs. 3, 5 and 7), accounting for the change in the sample emissivity, heat conductivity and heat capacity. Taking into account also the large uncertainty bands on emissivity values reported in [16], a constant emissivity of 0.5 was therefore assumed to be a reasonable approximation. The resulting additional error will not affect the current measurements, as no experimental data were measured in the liquid phase. Accurate measurements of emissivity in liquid carbides via polychromatic fast pyrometry are planned.

Fig. 8 shows a comparison between the average solidus–liquidus temperatures and solid–solid transitions obtained using laser melting, superimposed on the U-C phase diagram calculated using Thermocalc® software and the thermodynamic database, FUEL-BASE [4]. All results are in good agreement with the calculated phase diagram, considering the wide scatter of data presented in the literature. The average melting point value for UC, of 2781 K, is in good agreement with the optimised phase diagram value of 2799 K. In the case of $UC_{1.5}$ and UC_2, both apparent solidus and liquidus points have been graphed. The experimental values for $UC_{1.5}$ agree with the calculated data; however the solidus–iquidus region identified is larger (23 K) than the calculated region (which shows a solidus–liquidus region of just 0.2 K, so practically congruent melting). The values for UC_2 were somewhat higher than the calculated phase diagram, by approximately 40 K, with a solidus–liquidus gap of a few degrees only, which may not be distinguishable from the measurement uncertainty.

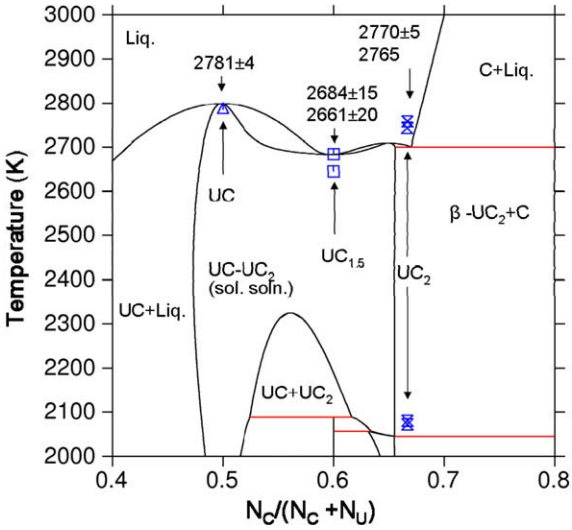

Fig. 8. Region of calculated U-C phase diagram, between $(N_C/(N_C + N_U))$ 0.4 to 0.8, showing average experimental data obtained using laser melting for the solidus–liquidus region and other solid–solid transitions.

From the experiments, the situation looks complex for compositions richer in carbon, i.e., $UC_{1.5}$ and UC_2. This behaviour suggests that probably higher uranium carbides do not melt congruently like UC, but rather through a solidus/liquidus scheme, which can lead to segregation phenomena if the cooling rate is too high, and hence to less well defined thermograms and more complex surface morphologies, as observed using the Reflected Light Signal and SEM. According to the assessed shape of the phase diagram, by Chevalier and Fischer [11] and Guéneau et al. [4], a eutectic point is certainly present between UC and UC_2. This point is probably located in the vicinity of the composition $UC_{1.5}$, for which the best defined thermal arrests were observed, corresponding to the lowest average liquidus point (2684 K), and a small liquidus–solidus gap (approximately 23 K). Benz et al. [8] suggest from their experiments, that a relative minimum point on the solidus line occurs for a C/U molar ratio of 1.6 ± 0.2 at 2653 K.

To summarize, congruent melting between UC and UC_2, certainly occurs at the composition UC, and near to the compositions $UC_{1.5}$ and UC_2. Further research, in the compositions ranges around the latter two stoichiometric carbides will be published in a forth coming paper.

The further transitions, observed for UC_2 are shown on the calculated phase diagram, and are in good agreement to the α-UC_2 to β-UC_2 solid–solid transition. Further experiments will be performed by laser heating samples below the melting point, combined with slower heating and cooling rates, in order to better study solid–solid phase transitions by this new method.

Table 2
Overview of experimental results from laser melting.

Samples	UC	$UC_{1.5}$		UC_2	
	T_m (K)	T_{sol} (K)	T_{liq} (K)	T_{sol} (K)	T_{liq} (K)
	2778	2661	2679	2765	2774
	2783	2665	2672	–	2765
	2776	2680	2685	–	2770
	2785	2638	2700	–	–
	2785	–	–	–	–
Average	2781 ± 4	2661 ± 20	2684 ± 15	2765	2770 ± 5

5. Conclusions

Laser heating, combined with Reflected Light Signal technique, was proven to be a suitable and promising methodology for the study of high temperature phase transitions in uranium carbides, for both solid–liquid and solid–solid phase transitions. Preliminary tests showed that fast laser heating experiments can be carried out on the uranium carbides, without risks of burning the specimen during testing. The melting point of UC was precisely measured (2781 ± 4 K), and obtained results confirm literature data, however

with greater accuracy. The melting behaviour of higher carbides was shown to be more complex, suggesting that a solidus–liquidus scheme is followed, probably even for UC_2, although with a very narrow gap.

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