

The UC_{2-x} – Carbon eutectic: A laser heating study



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H I G H L I G H T S

- The melting behaviour of nominal UC_{2.82} has been investigated.
- Temperature evolution of the sample emissivity has been observed.
- Surface carbon segregation in UC_{2.82} during cooling has been observed.

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The UC_{2-x} – carbon eutectic has been studied by laser heating and fast multi-wavelength pyrometry under inert atmosphere.

The study has been carried out on three compositions, two of which close to the phase boundary of the UC_{2-x} – C miscibility gap (with C/U atomic ratios 2 and 2.1), and one, more crucial, with a large excess of carbon (C/U = 2.82). The first two compositions were synthesised by arc-melting. This synthesis method could not be applied to the last composition, which was therefore completed directly by laser irradiation. The U – C – O composition of the samples was checked by using a combustion method in an ELTRA[®] analyser. The eutectic temperature, established to be 2737 K ± 20 K, was used as a radiance reference together with the cubic – tetragonal ($\alpha \rightarrow \beta$) solid state transition, fixed at 2050 K ± 20 K. The normal spectral emissivity of the carbon-rich compounds increases up to 0.7, whereas the value 0.53 was established for pure hypostoichiometric uranium dicarbide at the limit of the eutectic region. This increase is analysed in the light of the demixing of excess carbon, and used for the determination of the liquidus temperature (3220 K ± 50 K for UC_{2.82}). Due to fast solid state diffusion, also fostered by the cubic – tetragonal transition, no obvious signs of a lamellar eutectic structure could be observed after quenching to room temperature. The eutectic surface C/UC_{2-x} composition could be qualitatively, but consistently, followed during the cooling process with the help of the recorded radiance spectra. Whereas the external liquid surface is almost entirely constituted by uranium dicarbide, it gets rapidly enriched in demixed carbon upon freezing. Demixed carbon seems to quickly migrate towards the inner bulk during further cooling. At the $\alpha \rightarrow \beta$ transition, uranium dicarbide covers again the almost entire external surface.

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1. Introduction

If the higher fissile density constitutes a big advantage of actinide carbides as an alternative nuclear fuel to oxides, the uncertainties mostly linked to metastability and uncontrollable oxygen and nitrogen impurities still represent an obstacle to the fabrication and employment of these materials [1]. Moreover, the metallic thermal conductivity and high melting temperature of

actinide carbides ensures a higher conductivity integral margin to melting for these materials with respect to the traditional UO₂, UO₂–PuO₂ and ThO₂ fuels.

This feature, together with the better compatibility with liquid metal coolants of carbides compared to oxides, are further reasons making of them good alternative candidates for high burnup and/or high temperature nuclear fuel.

Uranium carbide was traditionally used as fuel kernel for the US version of pebble bed reactors as opposed to the German version based on uranium dioxide. For the Generation IV nuclear systems, mixed uranium–plutonium carbides (U, Pu) C constitute the primary option for the gas fast reactors (GFR) and UCO is the first

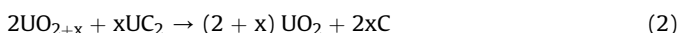
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candidate for the very high temperature reactor (VHTR). In the former case the fuel high actinide density and thermal conductivity are exploited in view of high burnup performance. In the latter, UCO is a good compromise between oxides and carbides both in terms of thermal conductivity and fissile density. However, in the American VHTR design, the fuel is a 3:1 ratio of $\text{UO}_2:\text{UC}_2$ for one essential reason, well explained by Olander [2] in a recent publication. During burnup, pure UO_2 fuel tends to oxidize to UO_{2+x} . UO_{2+x} reacts with the pyrocarbon coating layer according to the equilibrium:



The production of CO constitutes an issue in the VHTR because the carbon monoxide accumulates in the porosity of the buffer layer. The CO pressure in this volume can attain large values and, along with the released fission gas pressure, it can compromise the integrity of the coating layers and contribute to the kernel migration in the fuel particle (“amoeba effect”). In the presence of UC_2 , the following reaction occurs rather than reaction (1) in the hyperstoichiometric oxide fuel:



Because no CO is produced in reaction (2), this latter is more desirable than (1) in view of the fuel integrity. The simultaneous presence of UC_2 and pure carbon in the fuel assembly, however, creates the possibility of further reaction between the dicarbide and pure carbon, conceivably resulting in the formation of a eutectic in case of thermal excursion. The existence of metal carbide-carbon eutectics in metal-carbon binary systems is well known for decades. The U–C system, in particular, has been studied both theoretically and experimentally [3–7]. However, the existence of a UC_{2-x} –C eutectic has been more postulated on the basis of experimental information collected in the immediate vicinity of the $\text{C/U} = 2.00$ composition [1,8] and thermodynamic optimisation of the binary phase diagram [5] than observed in compositions more abundantly enriched in carbon.

A possible reason for such a lack of experimental information can be sought in the phase demixing, hindering homogeneous synthesis of carbides with a large excess of graphite with traditional synthesis methods such as powder metallurgy or arc melting.

In the current work, uranium dicarbide with a large excess of carbon (up to an atomic ratio $\text{C/U} = 2.8$) was obtained by melting uranium dicarbide in a graphite crucible in an induction furnace up to 2800 K under an inert atmosphere. The thus obtained carbide-carbon mixture was then heated beyond 3500 K by laser irradiation, in order to obtain, upon rapid cooling, a homogeneous material. Simultaneous detection of the sample's real temperature by a fast multi-wavelength spectro-pyrometer permitted, for the first time in our knowledge, sound identification of a liquidus temperature, followed by the eutectic/monotectic transition, and, at much lower temperature, the cubic-tetragonal solid-solid phase transition typical of uranium dicarbide. As a comparison, similar thermograms (temperature versus time curves) are presented for the compositions UC_2 and $\text{UC}_{2.1}$. In addition, analysis of the radiance spectra recorded during the thermal cycles yielded *in situ* estimation of the sample surface composition across the various phase transitions.

2. Experimental approach

2.1. Sample preparation and analysis

Uranium dicarbide buttons were prepared by cutting arc melted

and quenched drops without major difficulties [3]. In contrast, homogeneous samples with larger carbon content could hardly be prepared by the same technique due to the large and uncontrollable separation of pure, solid carbon from the melted phase. Carbon-rich samples were rather produced by directly melting up to 2800 K in an induction furnace under oxygen-free, inert gas flux (helium) $\text{UC}_{1.9}$ fragments placed at the bottom of a graphite cylindrical crucible. The crucible's bottom then resulted in a mixture of graphite and eutectic (Fig. 1a). This part was then further homogenised by laser heating it under inert atmosphere (Ar at 0.3 MPa). After fast quenching to room temperature (cooling rates of 10^4 – 10^5 K s^{-1}), the bottom part of the crucible became a reasonably homogeneous eutectic mixture of carbon and uranium dicarbide, with a large excess of carbon with respect to the exact eutectic composition. This latter has been established to be close to $\text{UC}_{2.00}$ [5]. The melted and re-frozen eutectic surface was then cut away from the rest of the crucible (Fig. 1b). Its exact chemical composition was obtained by crushing a small part of it into a fine powder successively measured in the infrared carbon dioxide analyser described below. By repeating several tests, a reproducible composition $\text{C/U} = 2.82 \pm 0.08$ was obtained with such an approach. The melted and re-frozen eutectic disks cut from the cylindrical graphite crucibles were then mounted again in the laser heating sample holder, and laser shot a few more times beyond melting, in order to study more accurately phase transitions occurring during the thermal cycles, and their repeatability over successive thermal cycles.

Two commercial ELTRA[®] analysers combined with a controlled-atmosphere combustion setup were employed to measure, respectively, the carbon and oxygen content of the current samples. The traditional approach is based on the combustion of a sample at high temperature that permits to form gaseous carbon dioxide (CO_2) from either the carbon or the oxygen contained in the specimen, depending on the atmosphere and the crucible material in which the measurement is carried out (Fig. 2). The measurement is then based on the measured IR absorption of the produced CO_2 at a characteristic wavelength (2640 cm^{-1} or $3.79 \mu\text{m}$) [9].

In order to measure the carbon content, the sample is placed in an Al_2O_3 crucible inside an electrical induction furnace and heated up to 3500 K under a flow of oxygen (99.99% pure). It is assumed that all and only the carbon from the sample reacts with oxygen to produce CO and CO_2 . These gases pass through a system of filters and catalysts to obtain only CO_2 which is measured by IR-absorption spectroscopy. The quantity of CO_2 analysed directly yields the carbon content of the sample.

In the same way, using a graphite crucible inside a resistance furnace and a helium flow, it is possible to measure the oxygen contained in the sample. In this case, it is assumed that all the oxygen contained in the sample reacts with the crucible during heating and forms CO and CO_2 . The final amount of CO_2 is quantitatively determined by IR spectroscopy and, in this case, all the measured CO_2 corresponds to the oxygen content in the sample. Both systems were calibrated with standard materials such as steel and U_3O_8 .

2.2. Laser heating and fast pyrometry setup

Details of the laser-heating setup used in this research have been reported in a previous publication [10], although the technique has been partially modified in the present work. During the shots, a carbide disk was mounted in a sealed autoclave under an inert atmosphere (slightly pressurised argon at 0.3 MPa), in order to minimise high-temperature oxygen contamination of the samples.

Thermograms were measured on samples laser heated beyond melting by a TRUMPF[®] Nd:YAG cw laser radiating at 1064.5 nm, the

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