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F-BRIDGE Project: Presentation of the thermodynamic modeling of the (U-Pu-C) system

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Thermochemical modeling of U,Pu carbides systems

- Work performed within the frame of the FBRIDGE Project

  Objective of the FUELBASE Project: To develop a thermodynamic database which will constitute a flexible tool to perform thermodynamic calculations on advanced fuel materials (oxides, carbides, nitrides fuels) for future reactors

- The U-Pu-C-O system

  Objective: In the context of Gas Fast Reactor (high operating temperature ~ 1273 K)

  > **Calculation of phase equilibria + vapour partial pressures**
  > **Optimisation of the processing and operating conditions**

  Optimisation of the U-Pu-C-O system:

  > **Binary and ternary sub-systems including (U-Pu-C) system**

    ↳ Binary sub-systems: U-Pu, U-C and Pu-C systems ↲

  > **Thermo-Calc Software : Optimisation with the CALPHAD method using available experimental data**

FUELBASE (2005-2011): Progress

Am	C	Cr	Mo	N	Nb	Np	O	Pu	Re	Ru	Si	Ta	Ti	U	V	W	Zr
Am						Kurata 10	Gotcu 10	Dupin 07						Kurata 10			
C	Andersson 87	Andersson 88	SGTE	Lee 01		SGTE	CEA 10	Dupin 07		Grobner 96	Frisk 96	Dumitrescu 98	Dupin 09	Huang 91	Jonsson 93	Guillermet 95	
Cr	Frisk 88	Frisk 91			Taylor 90	Dupin 06			Coughanowr 94		Saunders 98	Dupin 05	Lee 92			Zeng 98	
Mo	Frisk 91			Sundman 07	Dupin 05	Dupin 08		Liu 05		Chung 99	Dupin 06					Jerlerud 03	
N			SGTE	Sundman 05			Hillert 92		Jonsson 96	Chevalier 00	Ohtani 91			Ma 04			
Nb		Berche 09				Shao 04			Liu 08					Guillermet 91			
Np	Benes 09	Dupin 08					Kurata 10										
O	Gueneau 08			Hallsted 93		Sundman 05	Gueneau							Liang 01			
Pu	Berche 08	Dupin 08	Dupin 05	Berche 09	Dupin 06	Kurata 99	Berche 09	Berche 08	Kurata 99								
Re	Dupin					Berche 08		Dupin									
Ru						Dupin 08											
Si	Vahmas 89	Seifert 00	Berche 09			Vahmas 89	Guéneau 94										
Ta			Berche 09														
Ti	Rado 06	Saunders 98				Kumar 94											
U	Berche 09	Sundman 07	Chevalier 04														

Collaboration CEA, Calcul Thermo, ITU, NRG, ORNL

Ternary systems

U-Pu-O-C ➡ U-Pu-O, U-Pu-C, U-O-C, Pu-O-C

U-Pu-Am-Np-O ➡ U-Am-O, Pu-Am-O

U-Pu-Si-C ➡ U-Si-C

U-Pu-C-M ➡ U-Zr-C, U-C-Mo, U-C-Re, U-C-W, U-C-Nb , Pu-C-W

Pu-C-Mo , Pu-C-Nb , Pu-C-Re , Pu-C-Zr

C-N-Ti, C-Si-Ti, C-Mo-Ti, C-Mo-Si, U-Pu-Zr

C-Re-W, C-Re-Mo , C-Nb-Zr, U-Pu-Mo

The Thermo-Calc software

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- Calculations are performed with the Thermo-Calc software, developped in 1981(1) in order to optimize phase diagrams and perform various thermodynamic calculations. It is fairly well adapted for the description of non ideal systems (strong interactions between phases) and has been used to describe nuclear fuels in particular

(1) *N.Saunders and A.P. Miodownik ; CALPHAD (Calculations of Phase Diagrams) – A Comprehensive Guide ; Pergamon Materials Series (Volume 1) ; R. W; Cahn Editor (1998).*

- The optimisation of chemical systems is performed using the CALPHAD method (CALculation of PHAse Diagram) which takes into account all critically validated available experimental data

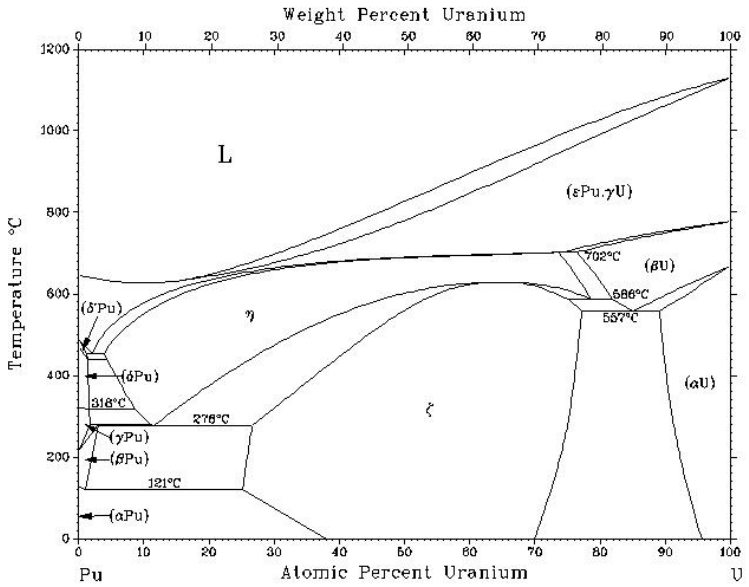
- The specificity of the method is the coupling between phase diagrams and thermodynamic properties in order to obtain a consistent full description of chemical systems

Binary description of the U-Pu system

- Binary sub-systems: U-Pu, U-C and Pu-C systems

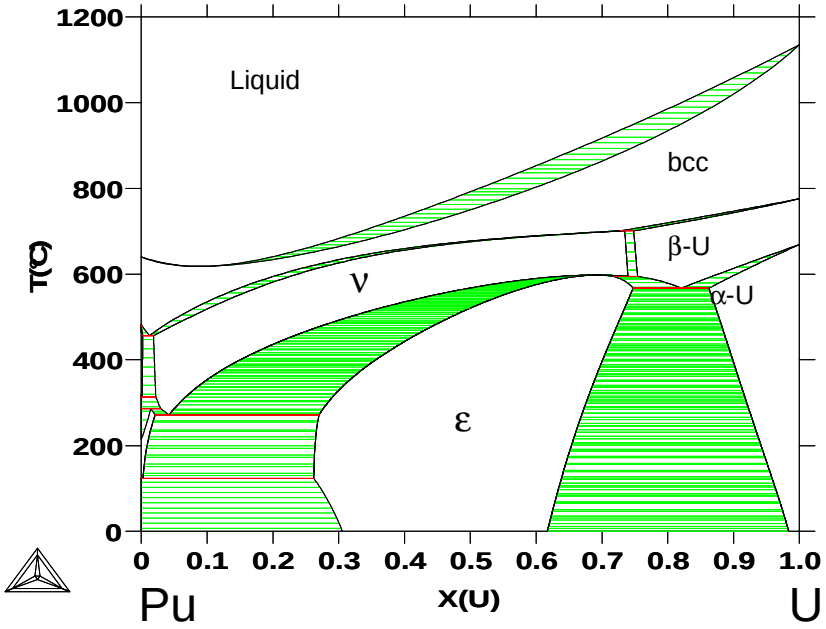
For the U-Pu System, the thermodynamic assessment from Kurata was used: *M. Kurata, CALPHAD 23 (1999), 305-337*

Kurata, Calphad 23 (3-4) (1999) 305-337



U-Pu phase diagram (Massalski's compilation)

Our calculation



Calculated U-Pu phase diagram

Binary description of the U-C system

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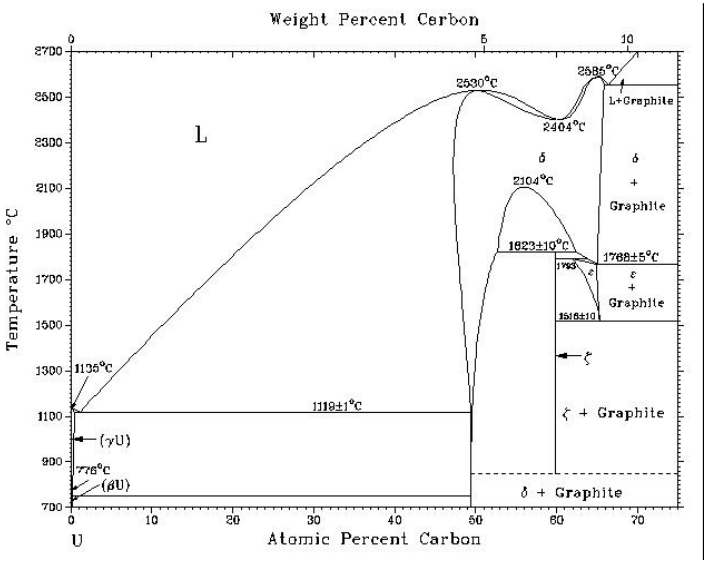
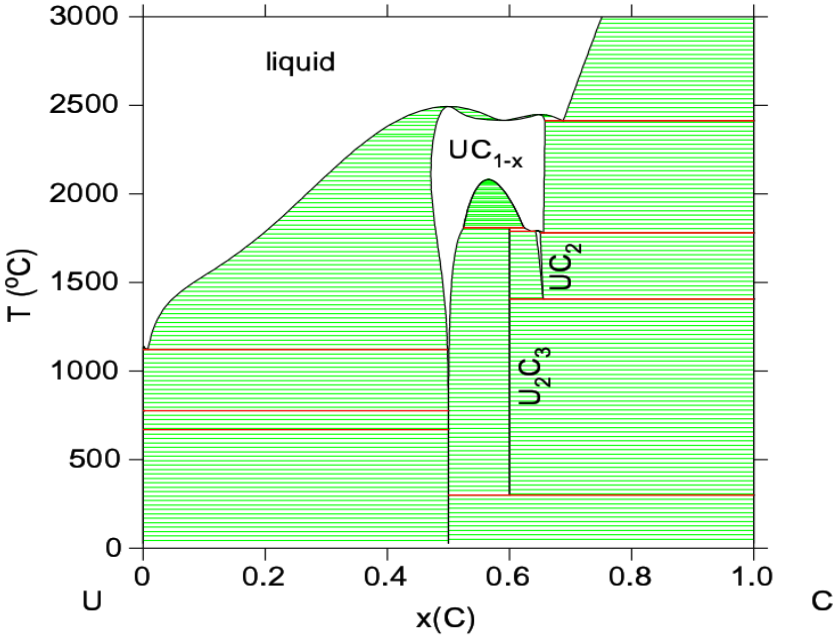
- U-C system → Thermodynamic assessment of *P.Y. Chevalier, E. Fischer, J. Nuc. Mat. 288 (2001), 100-129* ⇨

- problems with fcc U lattice stability, α-UC_2: Cp at low temperature
- underestimation of the UC_2 liquidus

☞ Re-assessment of N. Dupin, C. Gueneau and B. Sundman taking into account new experimental results (Laser heating + fast multi-channel pyrometry **from ITU** (Germany))



U-C phase diagram (Massalski's compilation)



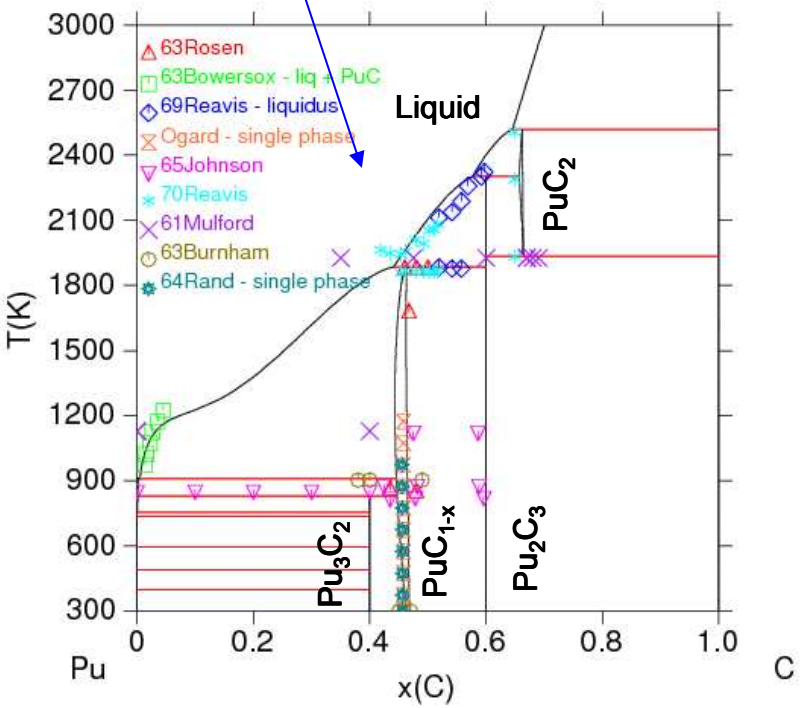
Calculated U-C phase diagram

Binary description of the Pu-C system

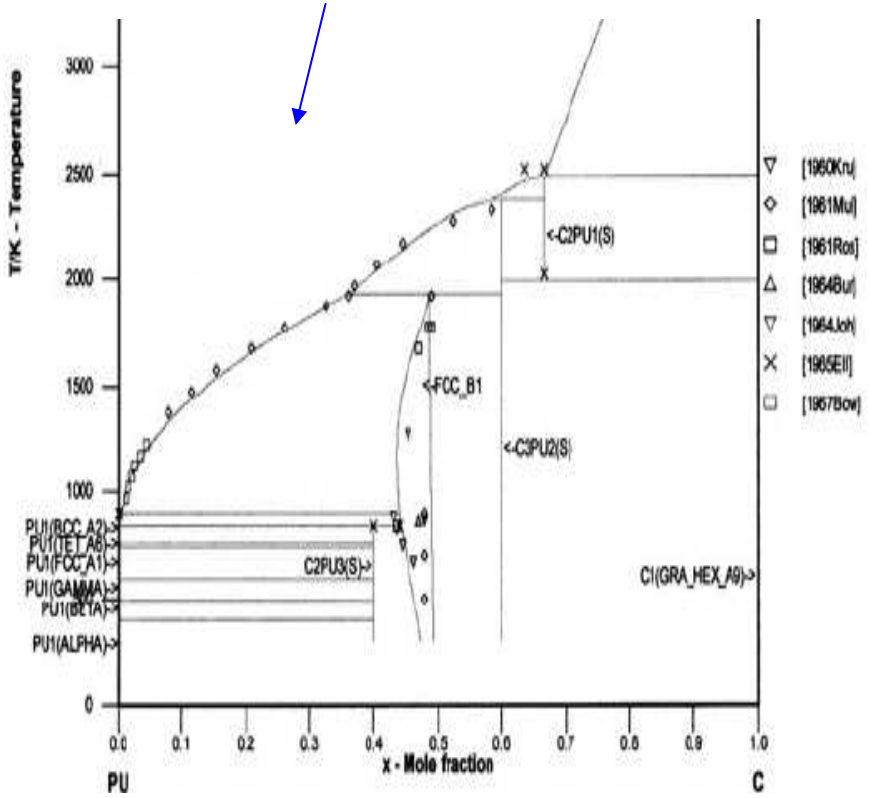
- Pu-C system → model of *E. Fischer, CALPHAD 32 (2008),371-377*
- New critical assessment of C. Gueneau, B. Sundman and C. Chatillon

Calculated phase diagram

Present work: PuC_{1-x} and β-PuC_2 described with a single model as in U-C



E. Fischer (CALPHAD 32 (2008) 371-377)

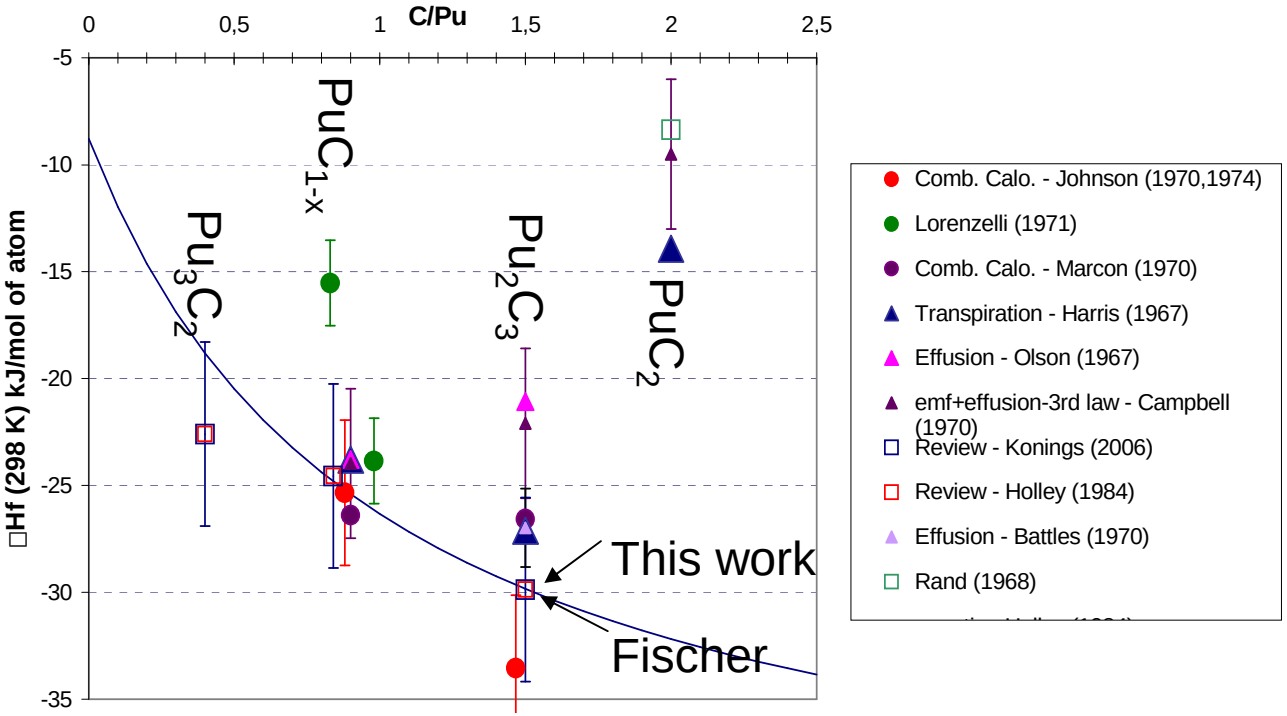


> The calculated phase diagrams are in good agreement

> Experimental data are missing (liquidus temperatures and data on PuC_2)

(Pu-C) system: ΔH_f(298.15K)

- Review of the enthalpy of formation data

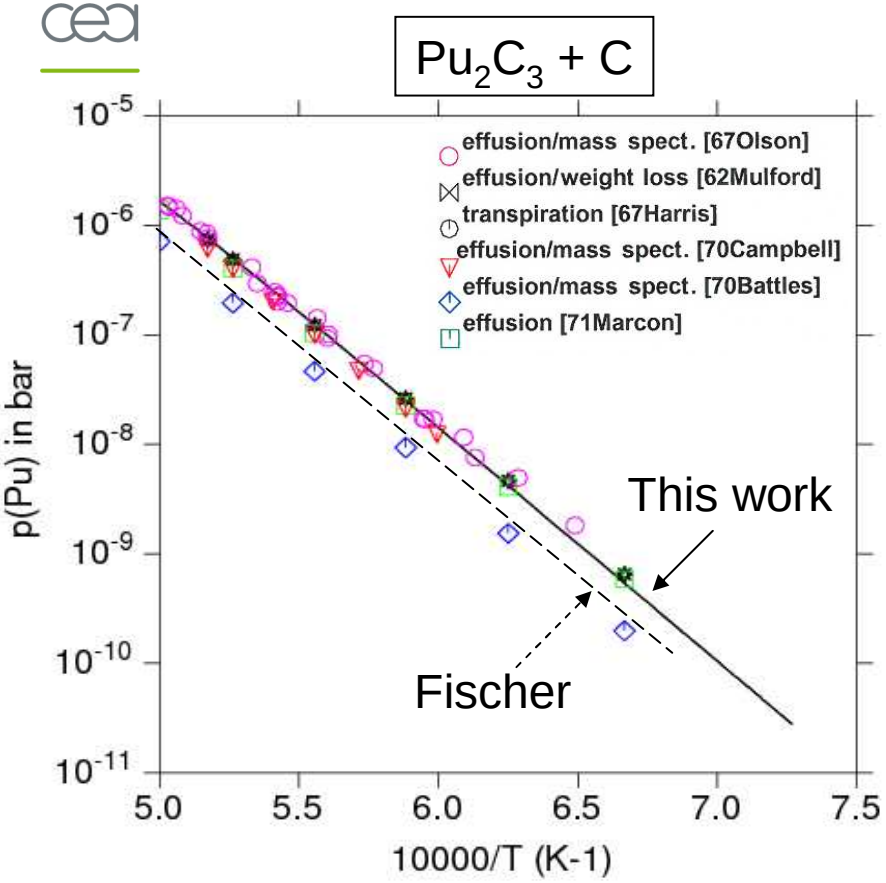


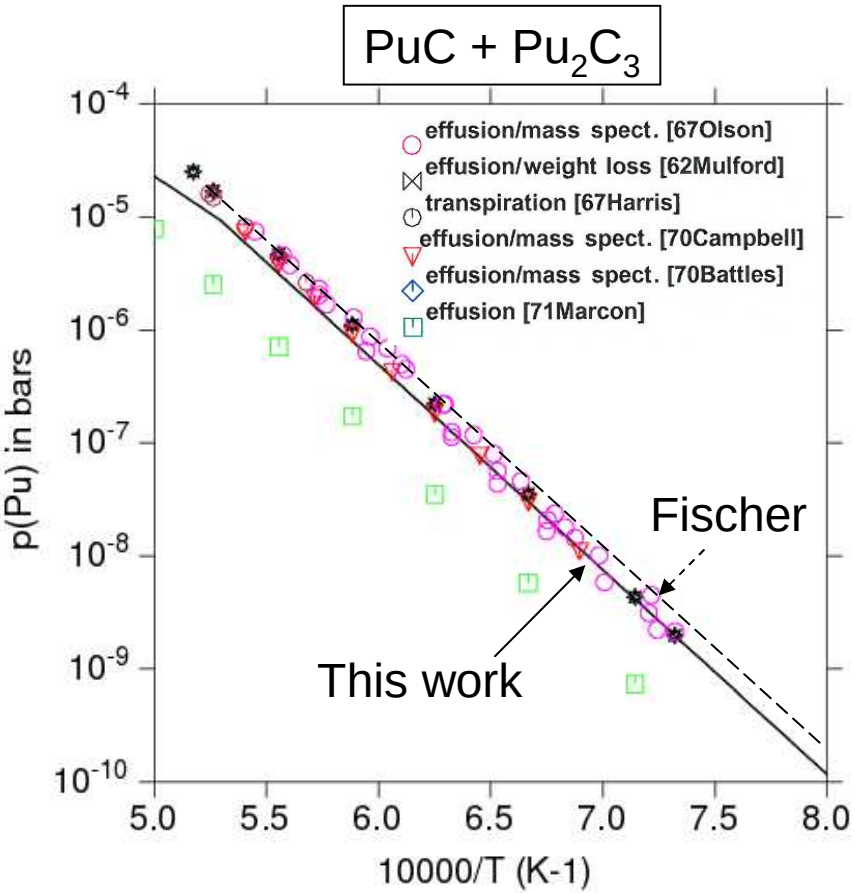
- The experimental data are scattered for Pu_2C_3
- In our assessment, we have looked at the partial pressure measurements to make a choice

  → Two sets of data for the P(Pu)g in two phase domains

(Pu-C) system: Partial pressure

- Review of the Pu partial pressure data in the two phase regions



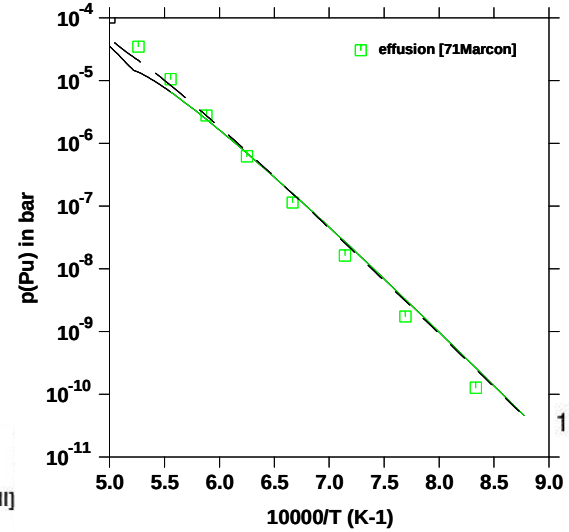


- In the present work, we have selected the higher values of p(Pu) that are consistent with:
  - Some exp. data of $\Delta H_f(Pu_2C_3)$
  - The $P(Pu_g)$ measurements in the ternary (U-Pu-C) system

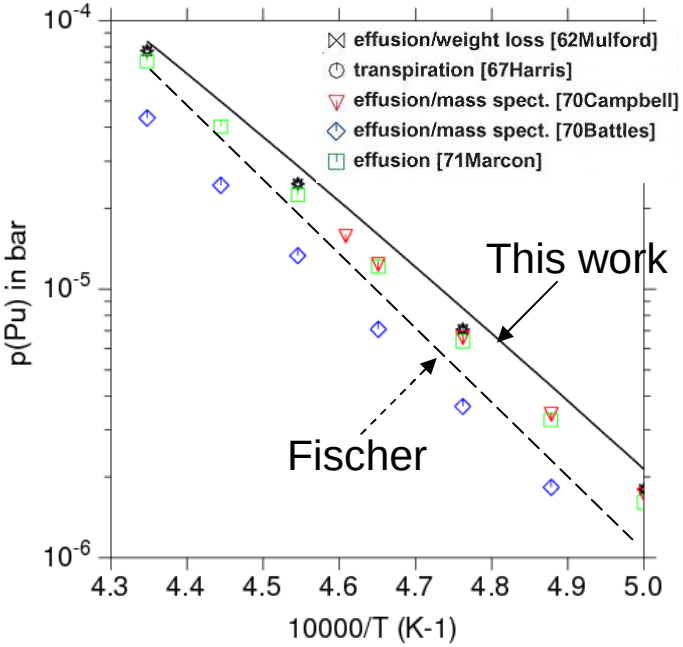
(Pu-C) system: Partial pressure

- Pu partial pressure data

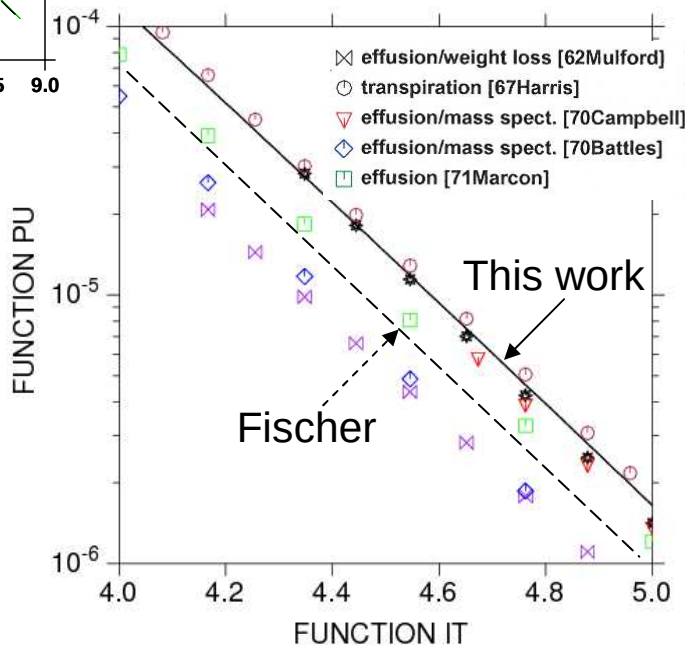
PuC + liq



$Pu_2C_3 + PuC_2$

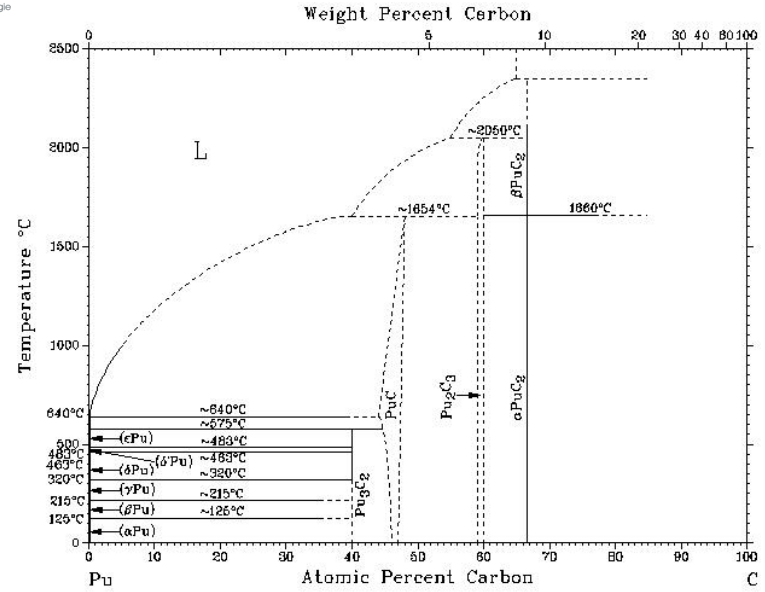


$C + PuC_2$

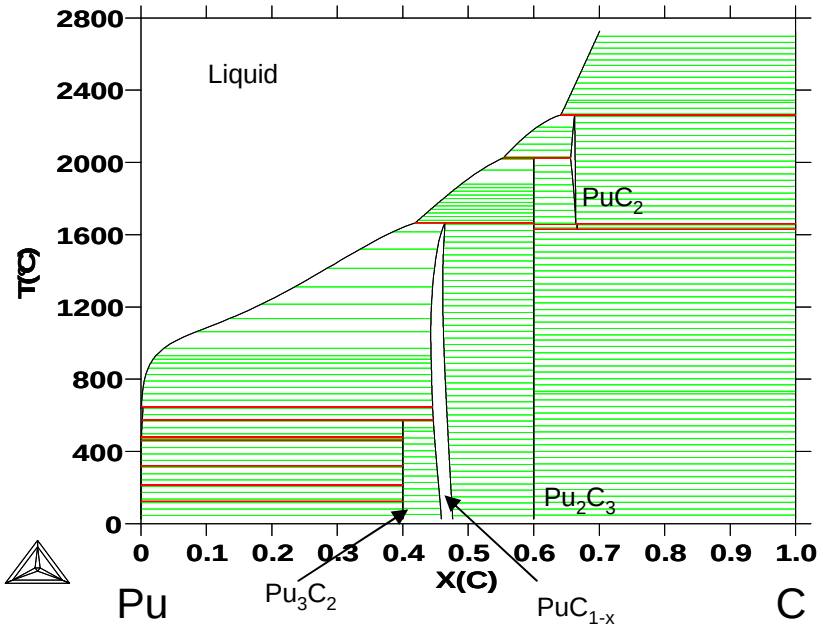


Binary Pu-C system: Phase diagram

- Pu-C system



- Pu-C phase diagram (Massalski's compilation)



- Calculated phase diagram

Thermodynamic description of the (U-Pu-C) system

- Extrapolation from the binaries

+ Ternary interaction parameters

Liquid (U,Pu,C)	L^0= +270000
Fcc $(U,Pu)_1(C_1,Va,C_2)_1$	L^0 (U,Pu)C = -55500 + 28 T L^0 (U,Pu)C_2= -32462 + 18.55 T

- "CEA" .TDB file ⇨

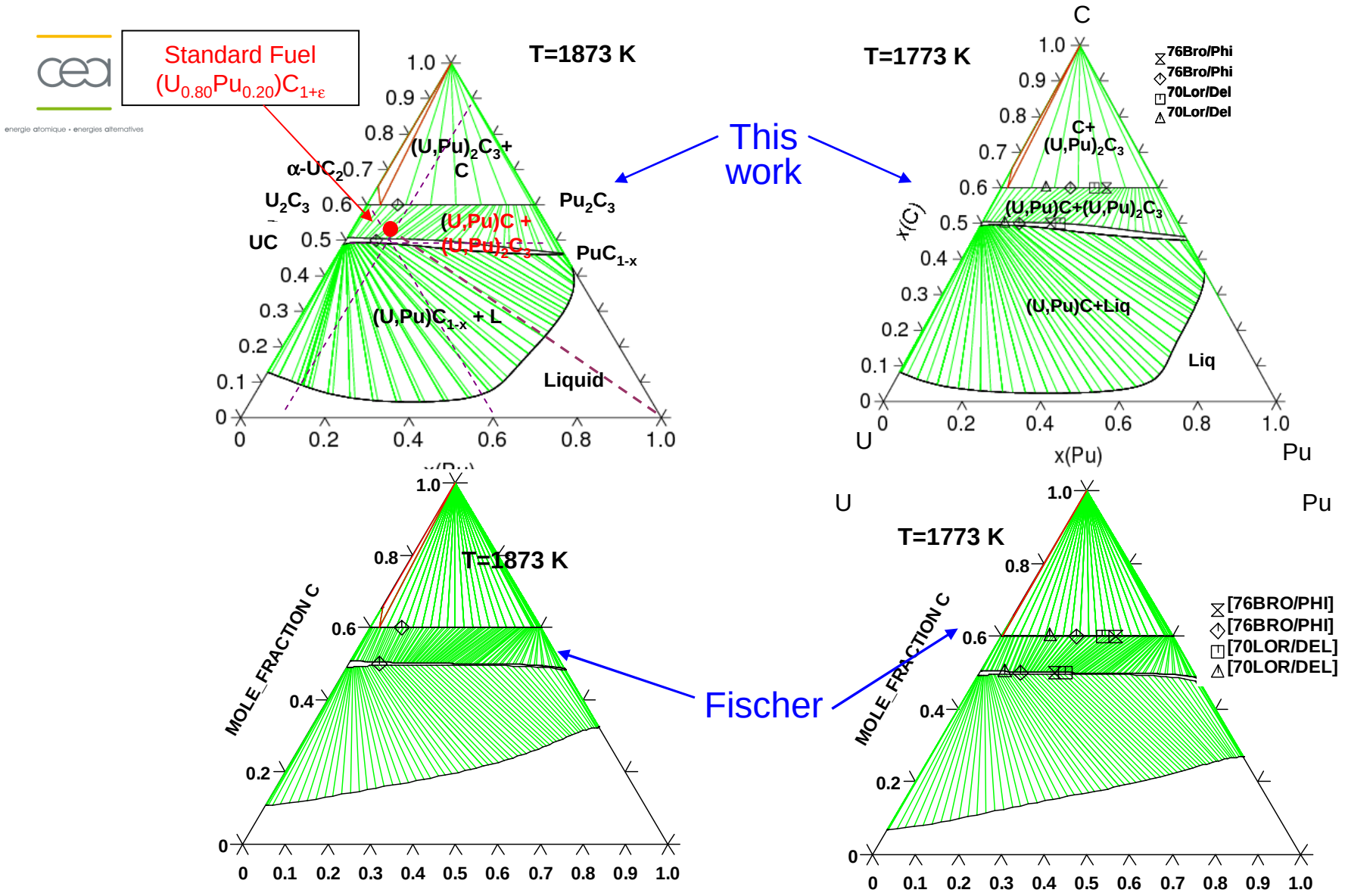
- Assessment of the U-Pu-C system published quite recently:

  → *E. Fischer, CALPHAD 33 (2009), 487-494* ⇨

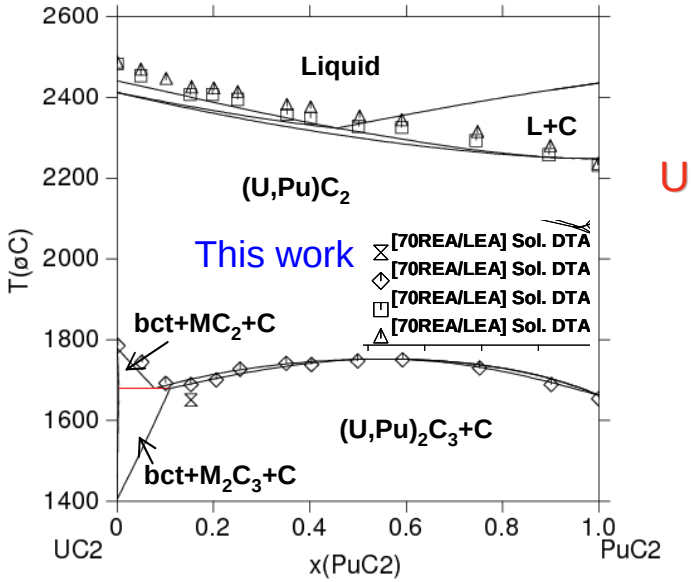
Comparison between both models:

Calculated Ternary system

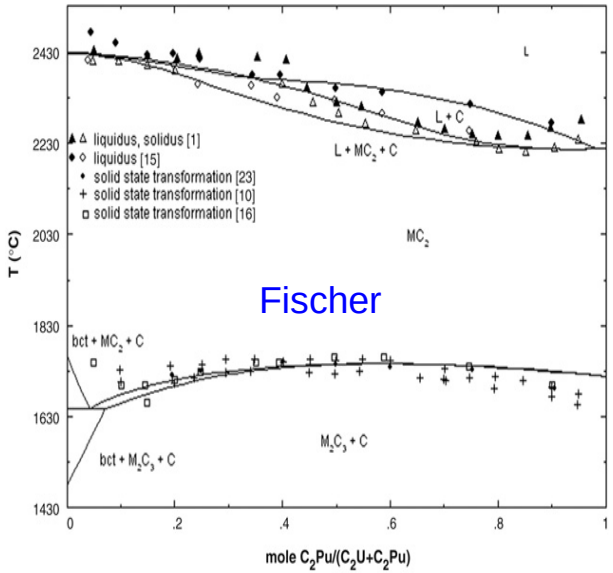
U-Pu-C system: Ternary sections

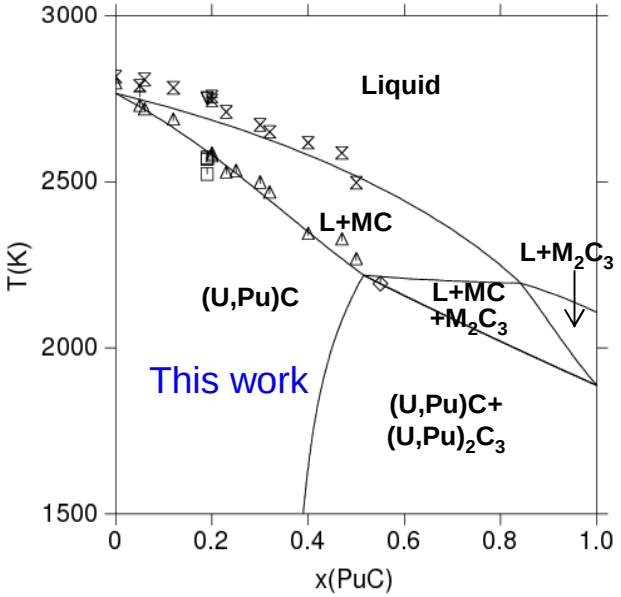


U-Pu-C system: Isopleth sections

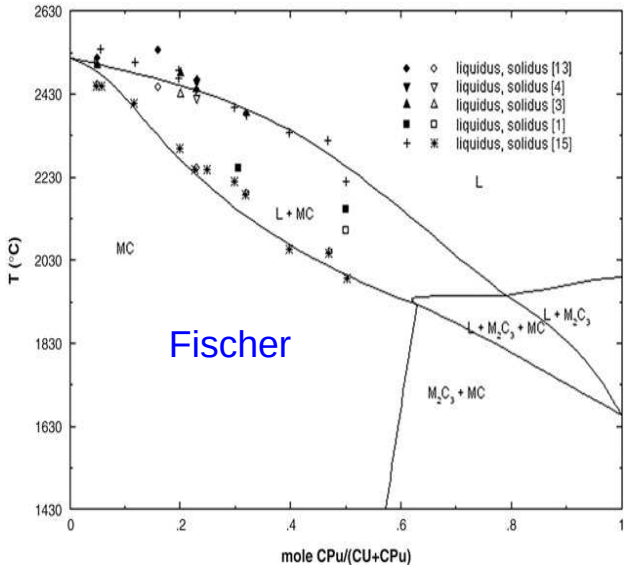


UC_2-PuC_2

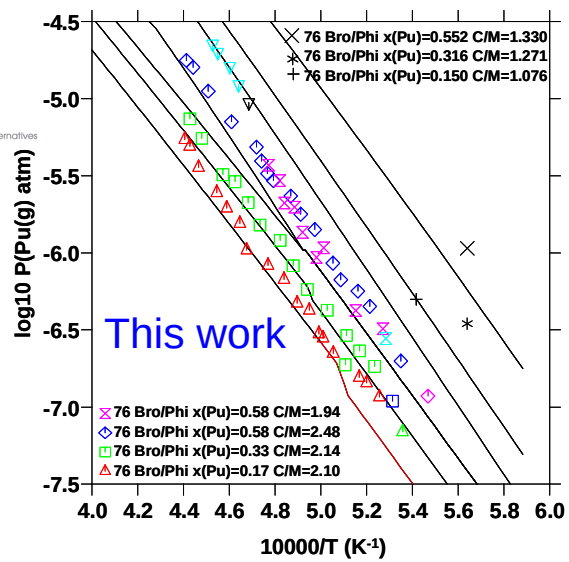


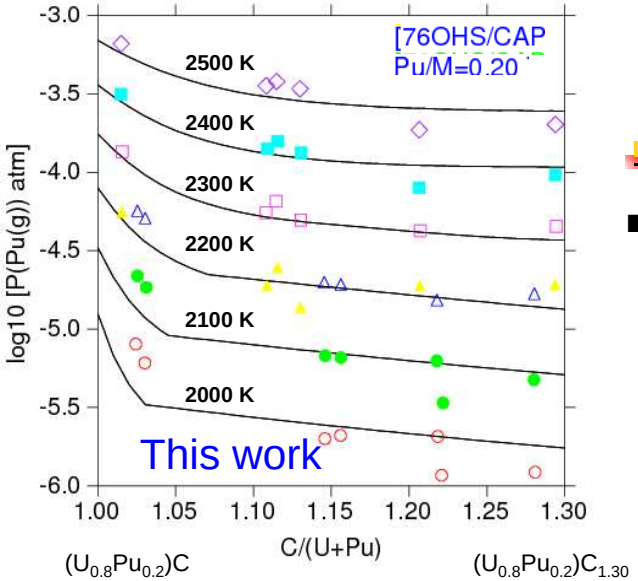


UC-PuC

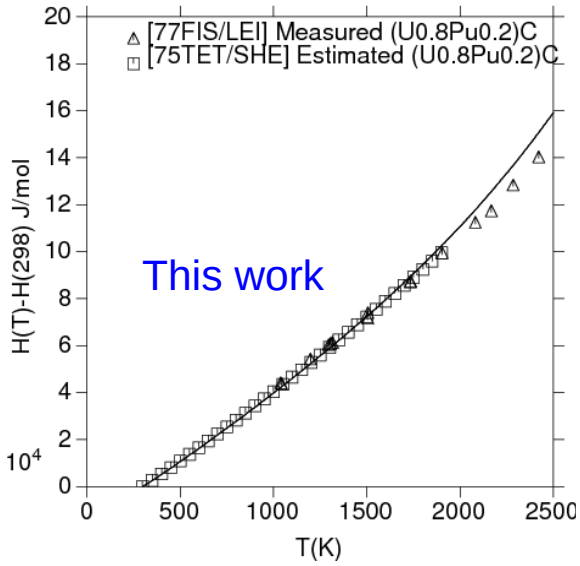


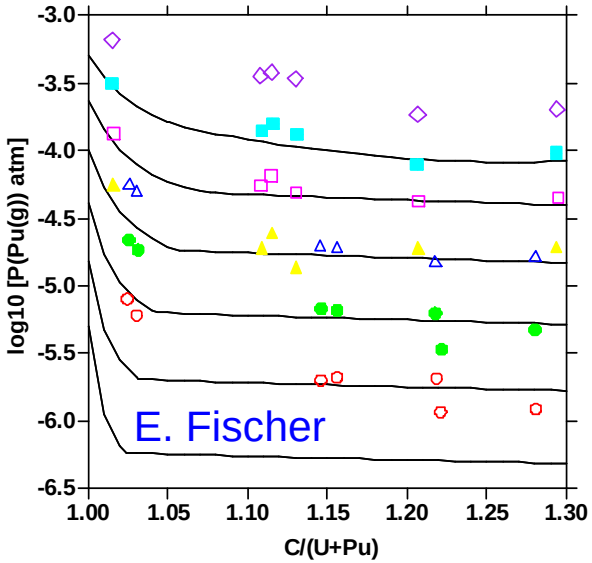
U-Pu-C system: Partial pressure





- Thermodynamic data
- ➡ A good agreement is obtained





The model of E. Fischer:
⇒ larger difference on the Pu partial pressure data

Conclusion – Outlooks

- Elaboration of a complete and reliable thermodynamic model of the (U-Pu-C) system:
  - > Phase diagram, vapor pressure, carbon potential of (U,Pu)C fuels
- Validity of the (U-Pu-C) database of the FUELBASE to describe the thermodynamic values of interest for fuel evaluation:

During fabrication:

- > Impurity specification for carbide fuel
- > Optimization of thermod. process parameters for fuel fabrication

During irradiation:

- > Effect of impurities on the thermochemical behaviour
- > Evolution of Carbon-to-Metal (C/M) ratio as a function of burn-up

Future work:

- Optimisation of the quaternary (U-Pu-C-O) system
- Some operational calculations:
  - > To define fabrication conditions limiting the oxy-carbides formation
  - > To estimate the Pu(g) loss during fuel manufacturing (carbothermic reaction) or during fuel operating conditions