



**KINETIC STUDY OF THE UO_2/C INTERACTION
BY HIGH TEMPERATURE MASS SPECTROMETRY**

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Kinetic Study of the UO_2/C Interaction by High Temperature Mass Spectrometry

Outline



1. Context & Needs
2. Subject approach
3. Chemical reaction between UO_{2+x} and graphite
4. High Temperature Mass Spectrometry
5. Samples Preparation
6. Experimental Measurements of $\text{CO}_{(g)}$ Release
7. Metallographic Analysis of the Samples
8. Kinetic Models
9. Conclusion

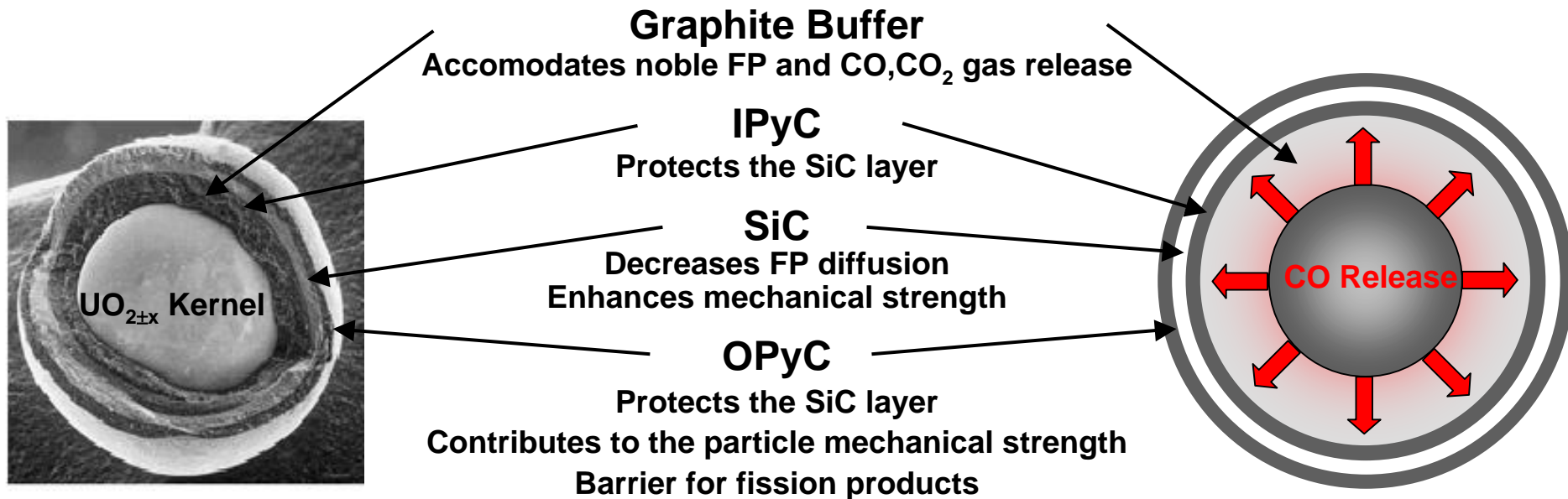
Kinetic Study of the UO_2/C Interaction by High Temperature Mass Spectrometry

Context & Needs



THERMOMECHANIC BEHAVIOR OF THE TRISO FUEL PARTICLE in HTR

Modelling the TRISO particle behavior under normal or accidental conditions due to $\text{UO}_{2\pm x}/\text{C}$ chemical interaction



ATLAS, a modelling code for

- Prediction of chemical interactions and CO, CO_2 formation
- Pressure values in the particle
- Also : *Release & Diffusion of Gas Fission Products*

Need of Input Data concerning the interaction between $\text{UO}_{2\pm x}$ and the Graphite Buffer

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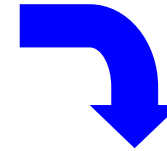
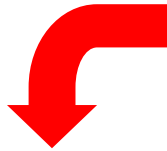
Subject approach



Evaluation of $\text{CO}_{(g)}$ pressure in the U-C-O system at high temperature
(1000°C-1600°C)

Stationary Equilibrium $\text{CO}_{(g)}$ Pressure
Variance of the System = 1

Unstationary $\text{CO}_{(g)}$ Pressure
Variance of the System $\neq 1$



THERMODYNAMIC Modelling (CALPHAD Method)
Reference for the Equilibrium $\text{CO}_{(g)}$ Pressures *

UO_2/C KINETIC (Experimental Measurements of $p_{(\text{CO})}$)
Determination of the Kinetic Interaction

- ⇒ *Constitution of an U-C-O Database*
- ⇒ *Critical Analysis of $\text{CO}_{(g)}$ Pressure*
- ⇒ *Phase Diagrams, Thermodynamic Properties*

- ⇒ *High Temperature Mass Spectrometry*
- ⇒ *Metallographic Analysis*



Thermomechanic behavior of HTR TRISO particle



* Review of $\text{CO}_{(g)}$ Pressure Measurements in the U-C-O Ternary System
Gossé S., Guéneau C., S. Chatain C., Chatillon C.
Journal of Nuclear Materials, 352, pp 13-21 (2006)

Kinetic Study of the UO_2/C Interaction by High Temperature Mass Spectrometry

Chemical Reaction between UO_{2+x} and graphite



First step: Case of a hyper stoichiometric UO_2



Second step: Case of an (under)-stoichiometric UO_2



Reduction of UO_{2+x}
No carbide phase formation

UO_2 Carbothermic conversion
Carbide formation

Known composition of the gaseous phase:
 $\text{CO}_{(g)}$ + few percents of $\text{CO}_{2(g)}$ (sometimes)

Expected carbide formation (UC , U_2C_3 , UC_2)

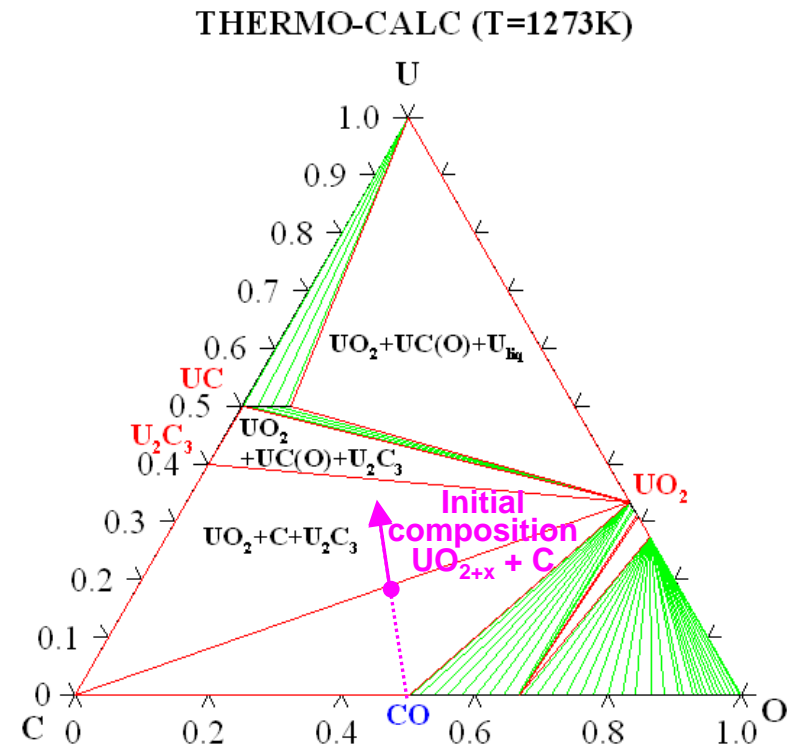
Kinetic predictive behavior:

Carbide = Function of the C/UO_2 ratio

- $\text{C}/\text{UO}_2 = 3$: Carbide = UC
 - $\text{C}/\text{UO}_2 = 4$: Carbide = UC_2
- (U_2C_3 is sluggish to be formed)

Thermodynamic predictive behavior:

- $T \leq 1650 \text{ K}$: Carbide = U_2C_3
- $T \geq 1650 \text{ K}$: Carbide = UC_2



Evolution of the overall composition in the UCO system

Kinetic Study of the UO₂/C Interaction by High Temperature Mass Spectrometry

High Temperature Mass Spectrometry



High Temperature Mass Spectrometry:

- High Temperature Mass Spectrometer
- Knudsen effusion cells

Measurements of Ionic Intensities of molecular beams according to the Hertz-Knudsen relation:

$$\frac{dn_i}{dt} = \frac{sCI_i T}{S_i \sqrt{2\pi M_i RT}} = \frac{sCI_i \sqrt{T}}{S_i \sqrt{2\pi M_i R}}$$

$$p_i S_i = I_i T$$

Rarefied gas flow:

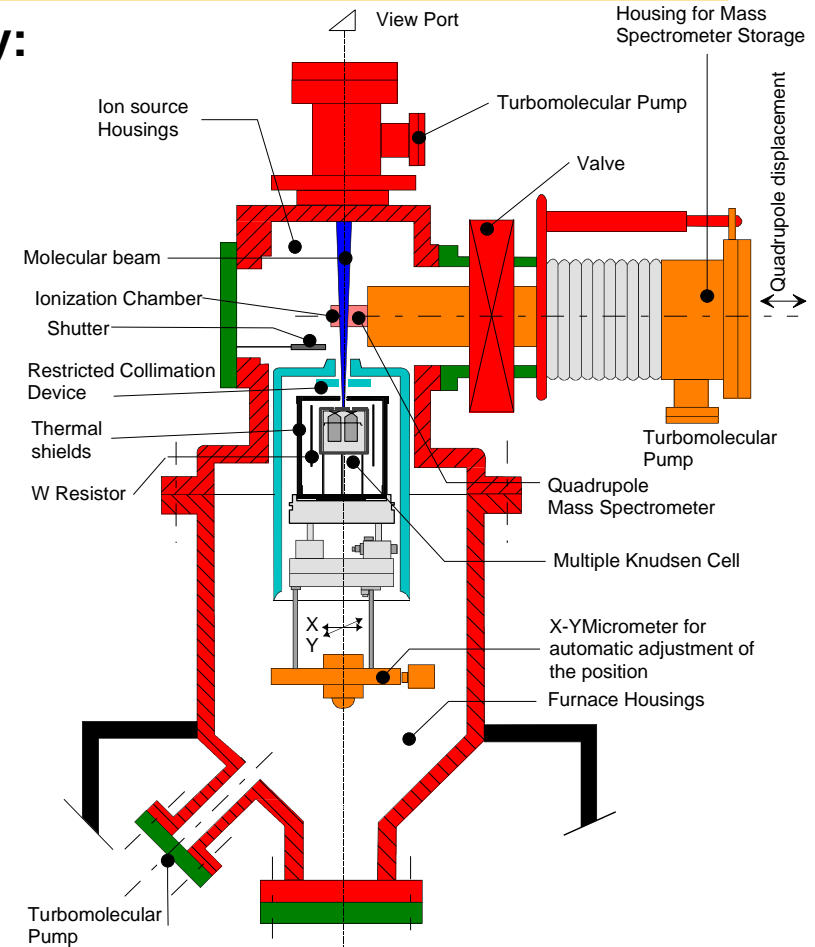
No shock between the ionized molecules during sampling
Representative of Thermodynamical Conditions

RESULTS:

- Partial Pressures
- Vapour Phase Composition
- Kinetics of Formation of the gas products CO_(g) and CO_{2(g)}

The total mass loss (Δm) is correlated with the gas products: CO_(g) and CO_{2(g)}
⇒ No need of any additional calibration of the spectrometer

Condensed phase composition measured from post-mortem analyse (SEM, XRD)
⇒ Determination of the final overall composition in the U-C-O system



Kinetic Study of the UO_2/C Interaction by High Temperature Mass Spectrometry

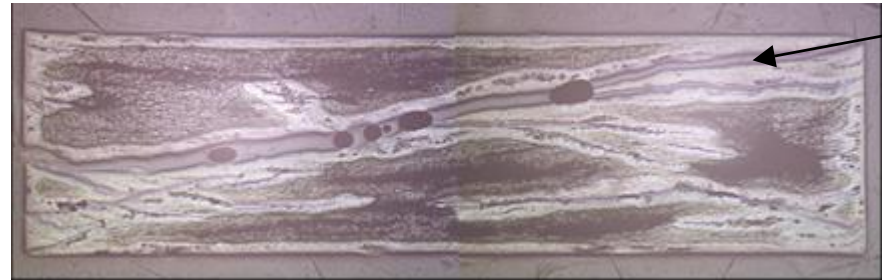
Samples Preparation



Mixture of UO_{2+x} (60% molar) and Graphite (40% molar)
Powders were packed and compacted in a glove box to form pellets



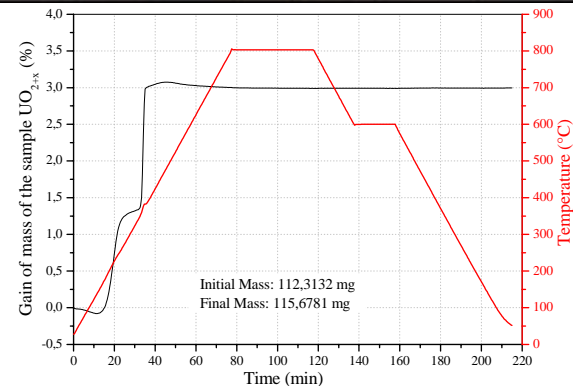
Shape of the ($\text{UO}_{2+x} + \text{C}$) green pellets
Cracks on the surface and in the bulk
(Optical Microscopy)



Crack

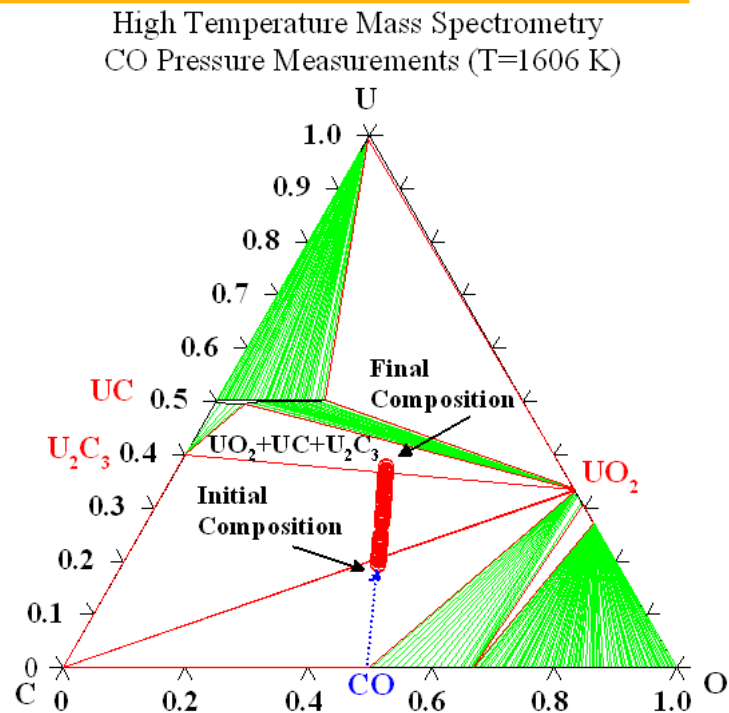
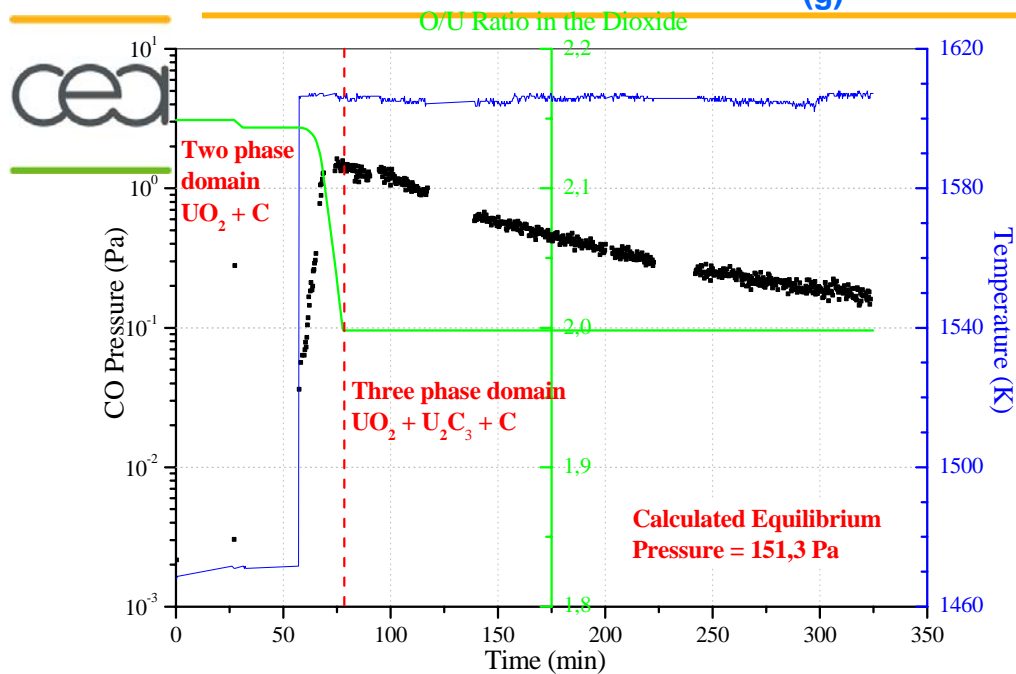
Determination of the Stoichiometry of UO_{2+x}
Thermo Gravimetric Analysis
Oxidation protocol of an UO_{2+x} green pellet into U_3O_8

Stoichiometry of $\text{UO}_{2+x} = 2.15$



Kinetic Study of the UO_2/C Interaction by High Temperature Mass Spectrometry

Experimental Measurements of $\text{CO}_{(g)}$ Release



End of the experiment in the three phase domain [$\text{U}_2\text{C}_3 + \text{UC} + \text{UO}_2$]

Lack of pressure plateau in spite of the variance of the chemical system ($V=1$)

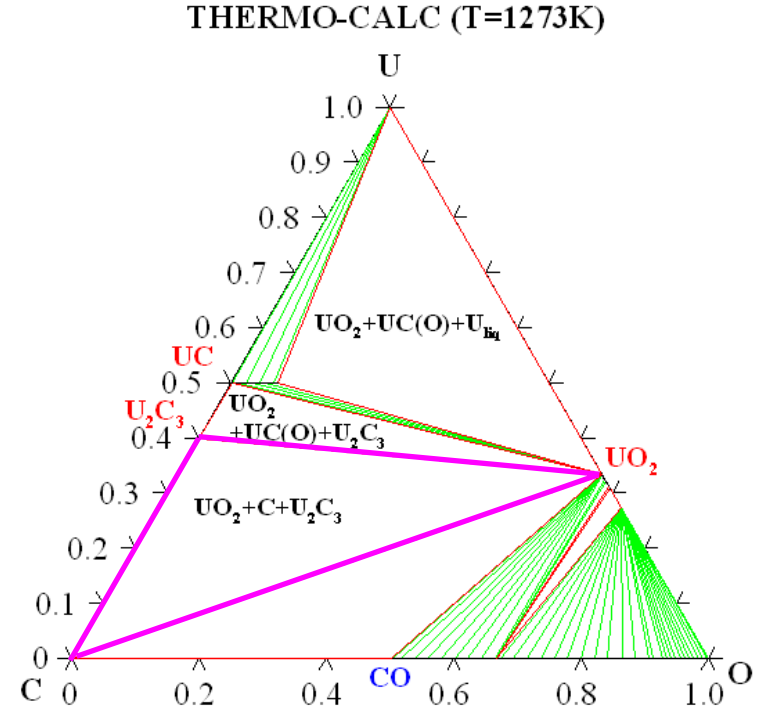
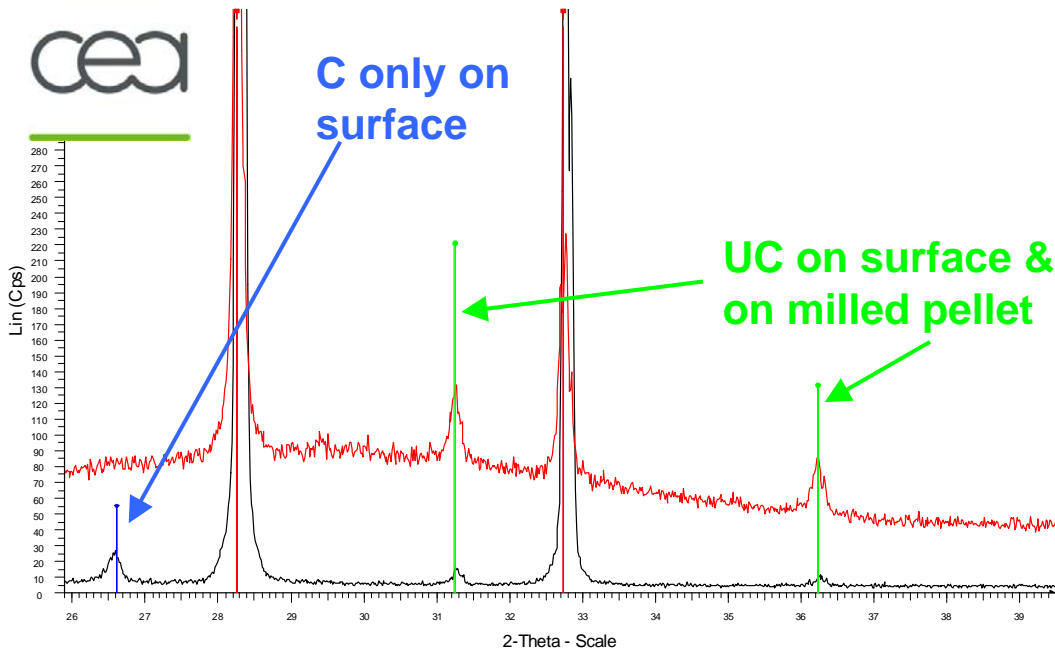
NO U_2C_3 : The formed carbide (UC) is not the Thermodynamical expected one

In the two-phase domain: The initial $\text{CO}_{(g)}$ rate increases until the composition reaches the theoretical [$\text{U}_2\text{C}_3 + \text{UC} + \text{UO}_2$] three-phase domain

As of the entry in the three-phase domain: Deceleration of the $\text{CO}_{(g)}$ formation rate

Carbide formation (U_xC_y) for $\text{O}/\text{U} \leq 1.998$
At the end of the experiment $P_{\text{exp}} = 25 \text{ Pa}$ and $P_{\text{exp}}/P_{\text{eq}} \approx 0.17$

Kinetic Study of the UO_2/C Interaction by High Temperature Mass Spectrometry Metallographic Analysis of the Samples



Optical Microscopy: Presence of a white phase INSIDE the UO_2 matrix (under the surface)

- Confirmation of the existence of three different phases [$\text{UO}_2 + \text{C} + \text{U}_x\text{C}_y$]
- Gradient of reactivity (different oxide stoichiometries $\text{UO}_{1.998} \leq \text{UO}_2 \leq \text{UO}_{2.15}$)
- Few graphite left in the pellet

X Rays Diffraction results: Confirmation of the existence of a carbide phase (UC)

- The amount of carbide is more important in the bulk
- The amount of carbon is more important on the surface

Final composition located at the frontier of the three-phase domaine [$\text{UO}_2 + \text{C} + \text{U}_2\text{C}_3$]

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Kinetic Models



Review of the Kinetic Models for the $\text{UO}_2 + \text{C}$ Interaction

Diffusion, Interface, Surface ???

Type of reaction controlling steps ???

- Solid – Solid
- Solid – Gas

Important Kinetic Parameters ???

- Relative Amounts of the Reagents
- Particle Sizing
- Geometry

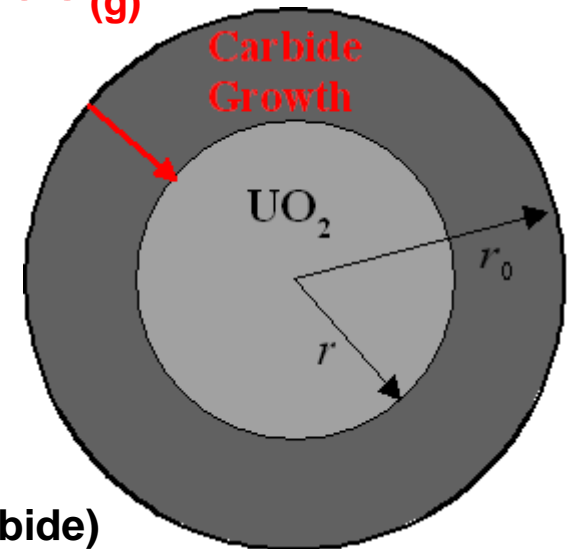


Retained Models:

- Diffusion (Valensi & Carter, Ginstling, Jander)
- Interface (Mukerjee)

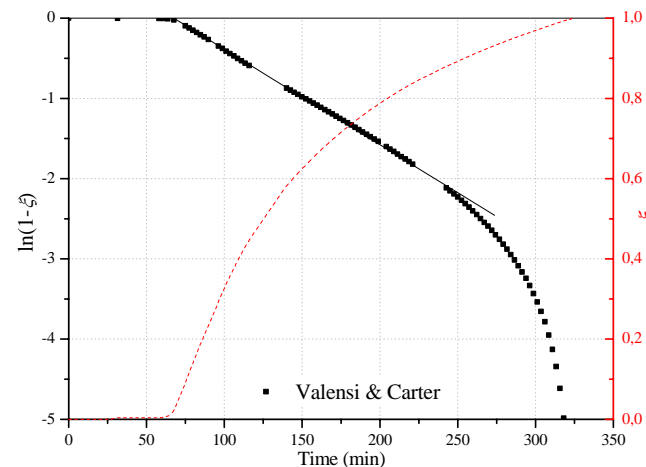
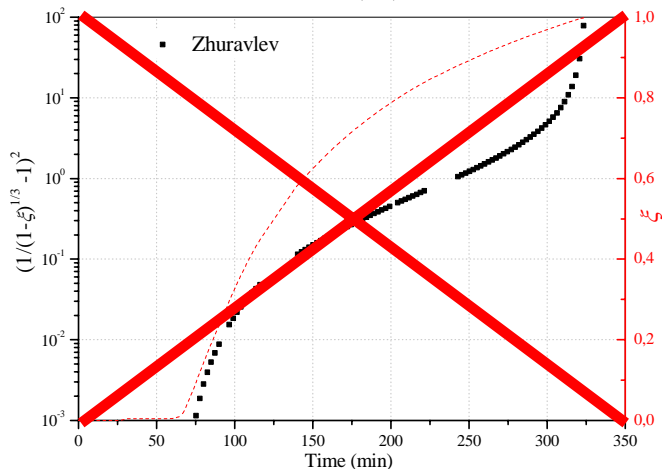
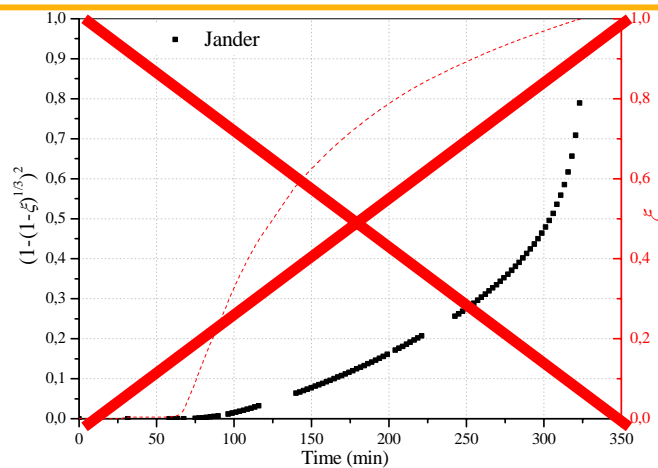
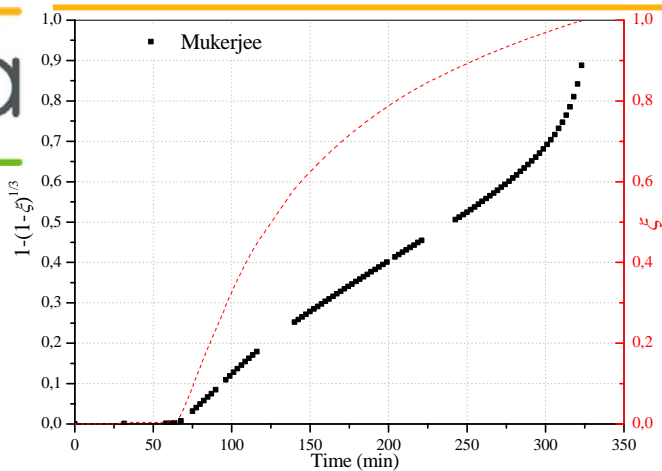
Assumptions:

- Centripetal growth of the products
- Spherical symmetry of the reagents and the products (carbide)
- Equivalent reactant-product molar volume (no volume expansion)



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Application of the Kinetic Models



- Processing of the $\text{CO}(\text{g})$ measurements is consistent for the Mukerjee's and Valensi's kinetic models
- Good agreement of Mukerjee's model due to close experimental conditions (samples, high vacuum)
- Lack of experimental data to conclude on the controlling kinetic mechanism

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Conclusions on the Interaction between UO_2 and C at High Temperature



HTMS Experimental Measurements of the $\text{UO}_2 + \text{C}$ interaction

Strong interaction between UO_2 and C for temperature above ≈ 1000 K

Main product of the interaction is $\text{CO}_{(g)}$

$\text{CO}_{2(g)}$ must be taken into account for $\text{O}/\text{U} \geq 2$ and for T lower than ≈ 1000 K

UO_{2+x} Reduction is characterized by two steps:

- Two-phase domain
Reduction of UO_{2+x} oxide without carbide formation (High rise of pressure)
- Three-phase domain
Formation of a carbide phase (Drop of pressure, no equilibrium after 5 hrs)

Kinetics Models

Best results obtained with the Mukerjee's and the Valensi's models

Reactional mechanism controlled by Interface and/or Diffusion phenomena ???

Carbide Formation: Carbide phase is function of the temperature

- $T \geq 1650$ K: Uranium Dicarbide (UC_2)
- $T \leq 1650$ K: Uranium Carbide (UC)

No trace of the predicted thermodynamic carbide: U_2C_3 – Too sluggish to be formed

Deviation from Thermodynamic Calculations

Experimental $\text{CO}_{(g)}$ pressure is largely lower than thermodynamic estimation

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PROSPECTS

Kinetic Study of the $\text{CO}_{(g)}$ formation during the $\text{UO}_2 + \text{C}$ Interaction

Need to perform longer experiments to obtain a pressure plateau in the three-phase domain

Experiments on UO_2 particles in a graphite bed

Experiments on UO_2 particles coated with graphite

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