A.P. Alexandrov Research
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"Phase Diagrams for Multicomponent Systems Containing Corium and Products of its Interaction with NPP Materials" (CORPHAD.2)

Presented by S. Bechta
11th CEG-SAM Meeting
March 6-9, 2007, Dresden

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CORPHAD project general information

Project participants and coordination

	Project Development Grant #1950.1	CORPHAD project #1950.2
Project duration	9 months	41 months*
Financial parties	Europe	Europe
Project status	Completed	Completed

CORPHAD project focus

- **Project objective:**

  Experimental study of phase diagrams of corium/NPP material mixtures

- **Experimental data output**

  - ***Liquidus and solidus temperatures versus components concentration***
  - ***Temperature-concentration regions of the miscibility gap***
  - ***Coordinates of eutectic, dystectic and other characteristic points***
  - ***Solubility limit of solution phases***

- **Data application**

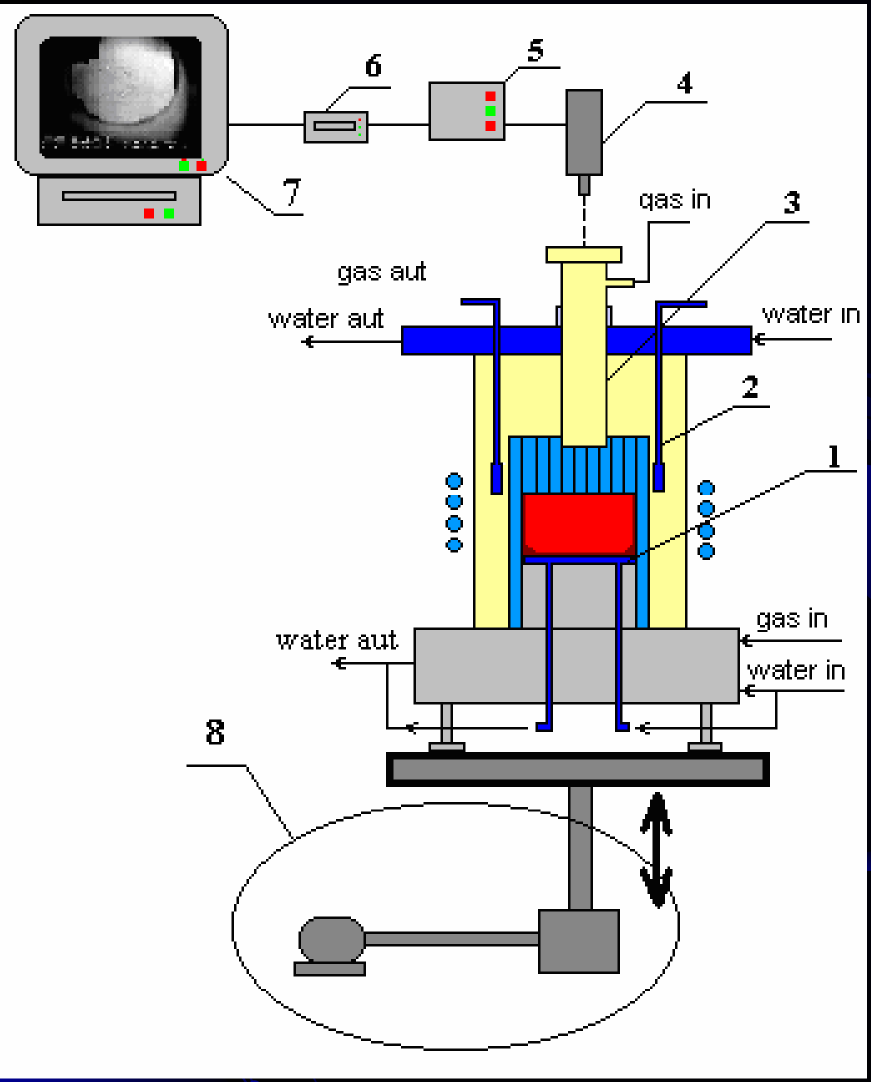
  - ***Thermodynamic database optimisation***
  - ***Thermodynamic code validation***
  - ***Corium behaviour modelling***

CORPHAD.2 project test matrix

Composition	Atmosphere	Experimental data
UO_2 – FeO	Argon/Helium	liquidus, solidus, solubility limits, eutectic points
ZrO_2 – FeO		
SiO_2 – Fe_2O_3/Fe_3O_4	Helium/Air/ Oxygen	liquidus, solidus, miscibility gap, eutectic points
UO_2 – SiO_2	Argon	miscibility gap
UO_2 – ZrO_2 – FeO/Fe_2O_3	Argon/Air	ternary eutectic points
U – O	Argon	liquidus, solidus, miscibility gap
U – Zr – O		
Zr – Fe – O		
U – Fe – O		
Complex corium mixture UO_2 – SiO_2 – ZrO_2 – Al_2O_3 – CaO – FeO – Cr_2O_3	Nitrogen	liquidus, solidus

Methodology: liquidus and solidus temperature determination

- **Visual polythermal analysis in the cold crucible (VPA IMCC)**

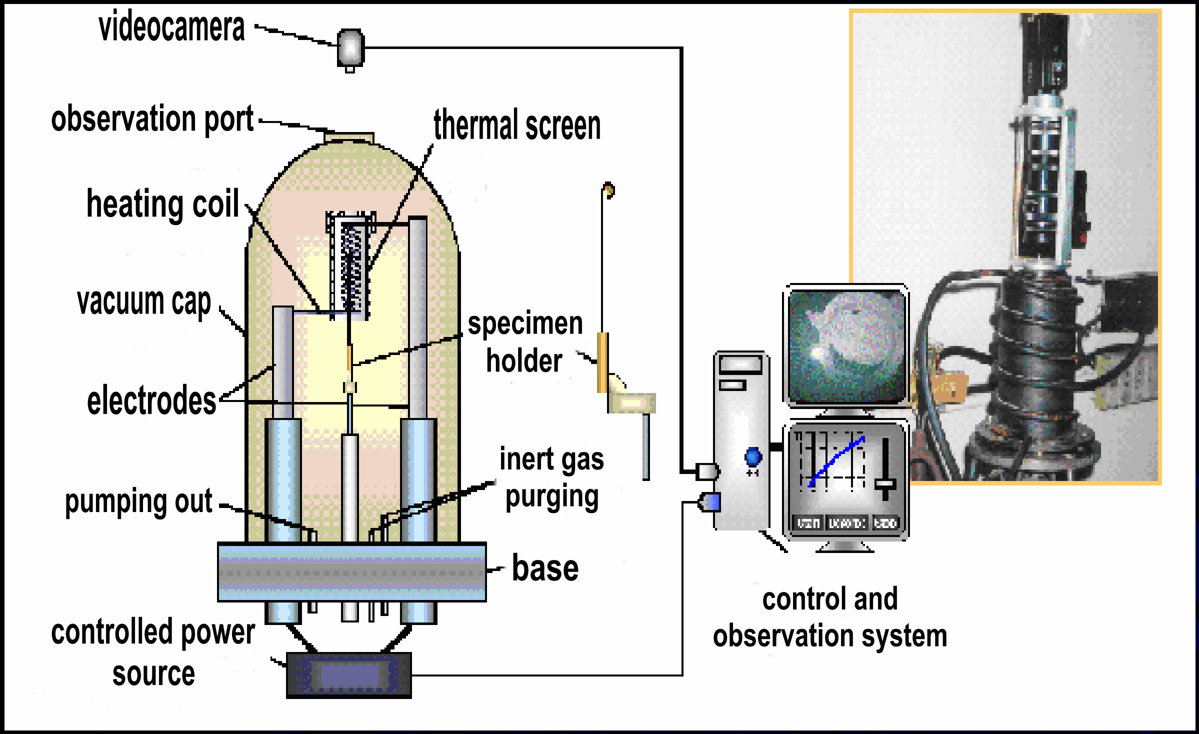


- **Formation of molten pool of specified composition**
- **Melt sampling**
- **Local cooling of surface layer of superheated pool by crucible lifting against inductor coil or by the layer shielding**
- **Surface temperature measurement of the melt coexisting with solid phase nucleus**
- **Transient to initial superheated conditions and repetition of measurements**

1 – Bottom calorimeter
2 - Movable water-cooled electromagnetic screen
3 - Pyrometer shaft
4 - Pyrometer couple with video camera,
5, 6 – DAS
7- Monitor/videotape recorder
8- Crucible vertical drive

Methodology: liquidus and solidus temperature determination

- Visual polythermal analysis in the Galakhov microfurnace



Test parameters:

Temperature up to 2500oC

Vacuum (10-5 - 10-6 atm) or inert gas atmosphere (He, Ar up to 2 atm)

Maximum heating rate – ca. 200 K/s

Specimen holder material – tungsten, iridium

Specimen weight – 100-200 mg

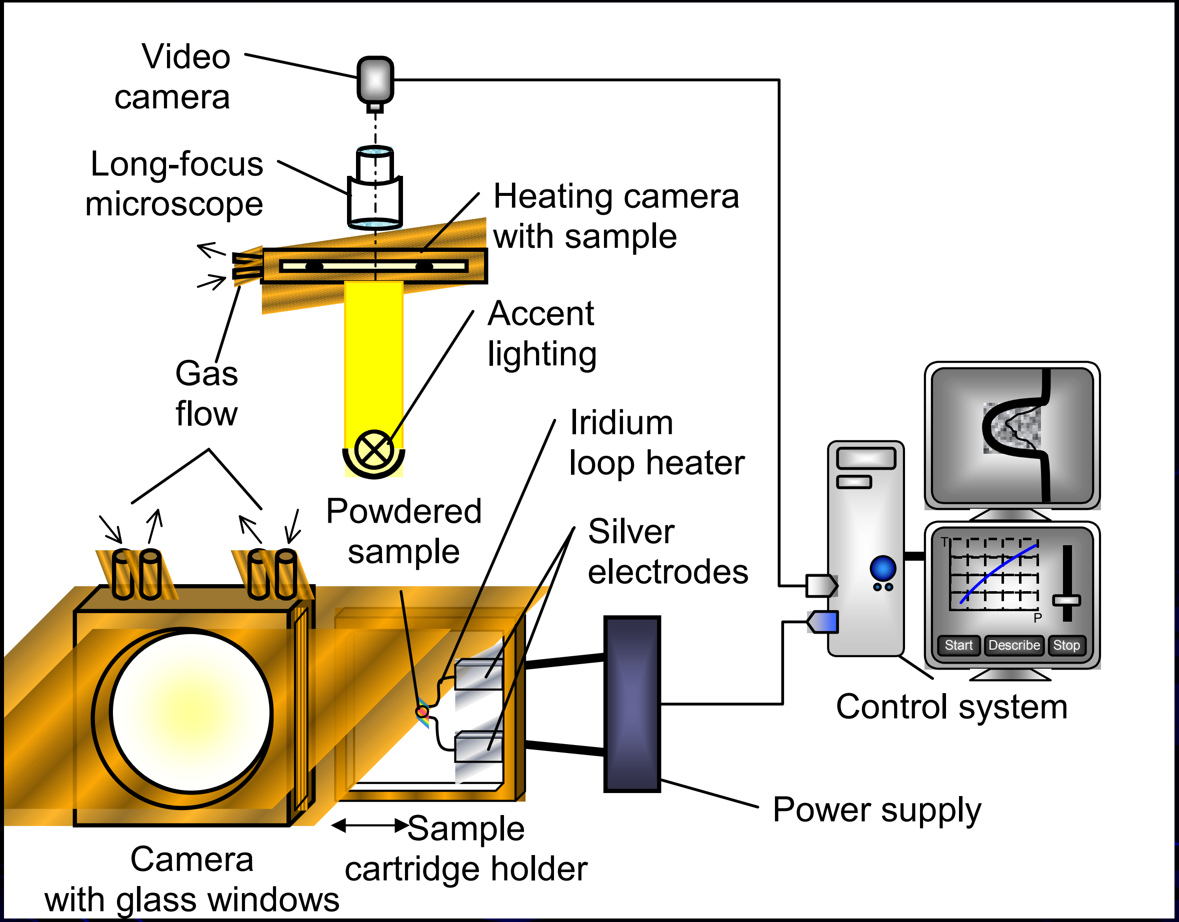
τ heating ~10 s

τ melting ~0.1s

- Calibration by using reference substances (Pt; Pd; Ag; Au; Al_2O_3 etc.)
- Heating is controlled automatically; the heating/cooling curve is specified
- Tsol and Tliq are fixed at the beginning of first liquid formation and of melt spreading across the tungsten (iridium) holder
- The maximum error of the method ± 50 °C

Methodology: liquidus and solidus temperature determination

- Visual polythermal analysis in the High-temperature microscope (HTM)



Temperature up to 2400°C

Air, oxygen, inert gas (He, Ar) with controlled oxygen partial pressure (p_{O2}=10^{-18}–1 atm)

Sample holder material – iridium

Sample weight – 10-50 mg

Methodology: liquidus and solidus temperature determination

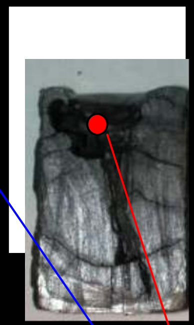
TG, DTA and DSK measurements:
SETERAM SETSYS evolution thermoanalyser

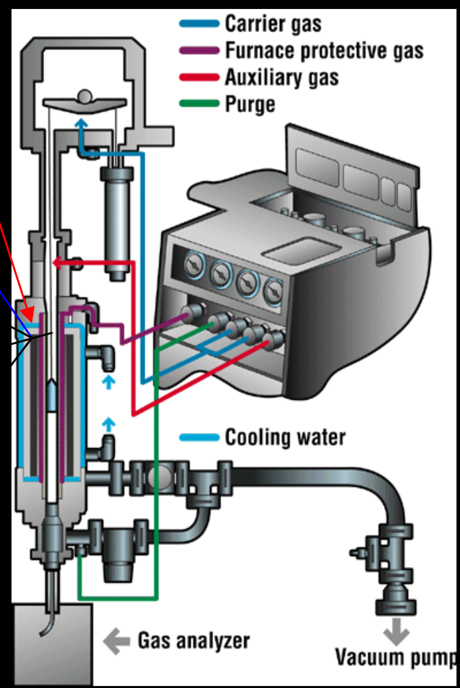
DTA:
Up to1500 ^{0}C
Up to 1600 ^{0}C
Up to 1750 ^{0}C
Up to 2400 ^{0}C

TG-DTA:
Up to 1500 ^{0}C
Up to 1600 ^{0}C
Up to 1750 ^{0}C
Up to 2400 ^{0}C

DSK:
Up to 1500 ^{0}C
Up to 1600 ^{0}C

TG-DSK:
Up to 1500 ^{0}C
Up to 1600 ^{0}C





To be determined:

- **T_{sol} and T_{liq}**
- **Phase transition temperatures**
- **Enthalpy**
- **Specific heat**
- **Phase transition heat**
- **Thermogravimetry**

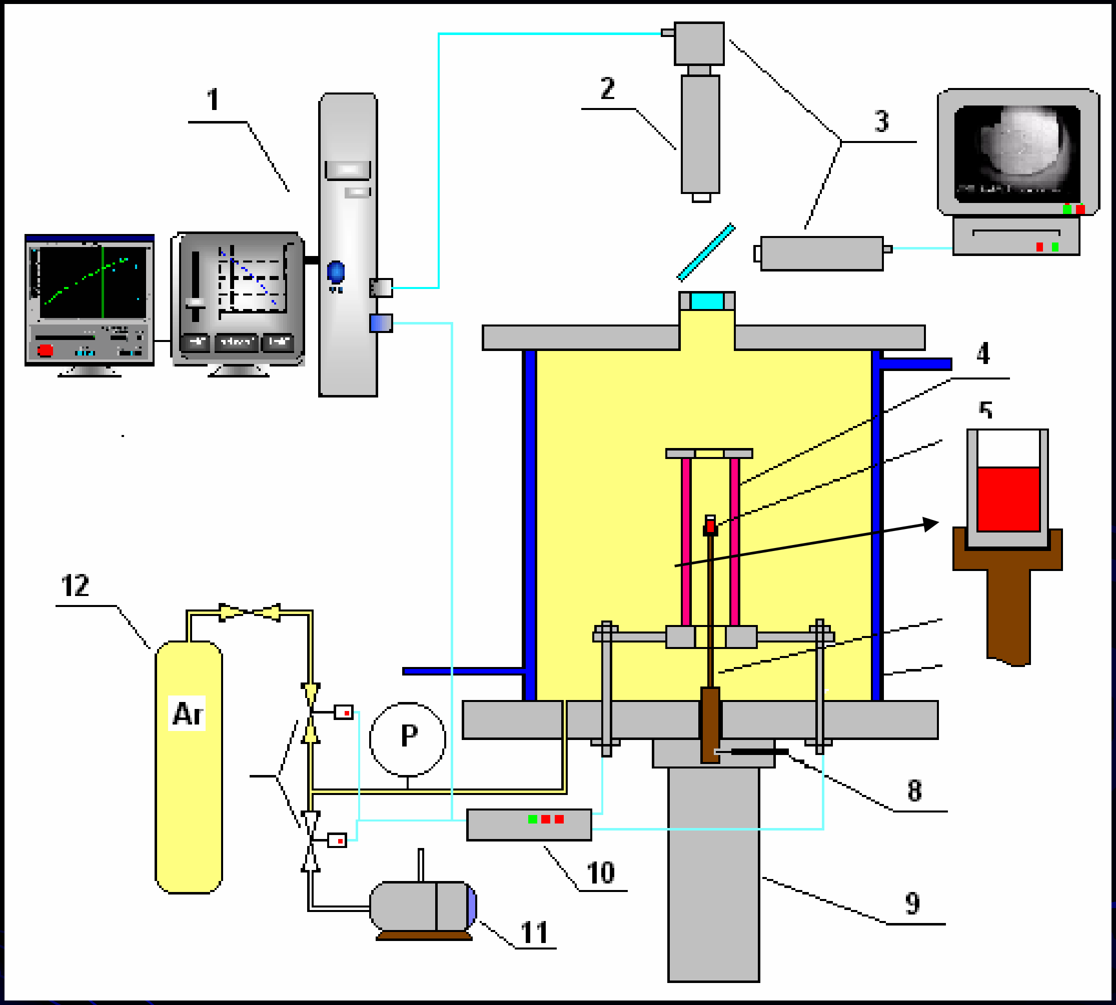
Variable parameters:

- **Specimen heating rate**
- **Furnace atmosphere - N_2, He, Ar, CO_2, air, gas mixture**
- **Vacuum**
- **Furnace pressure**

- Specimens are prepared from the IMCC
- T_{sol} and T_{liq} are determined by the endothermal effect onset at the specimen heating

Methodology:annealing at different temperatures and quenching

Radiant microfurnace

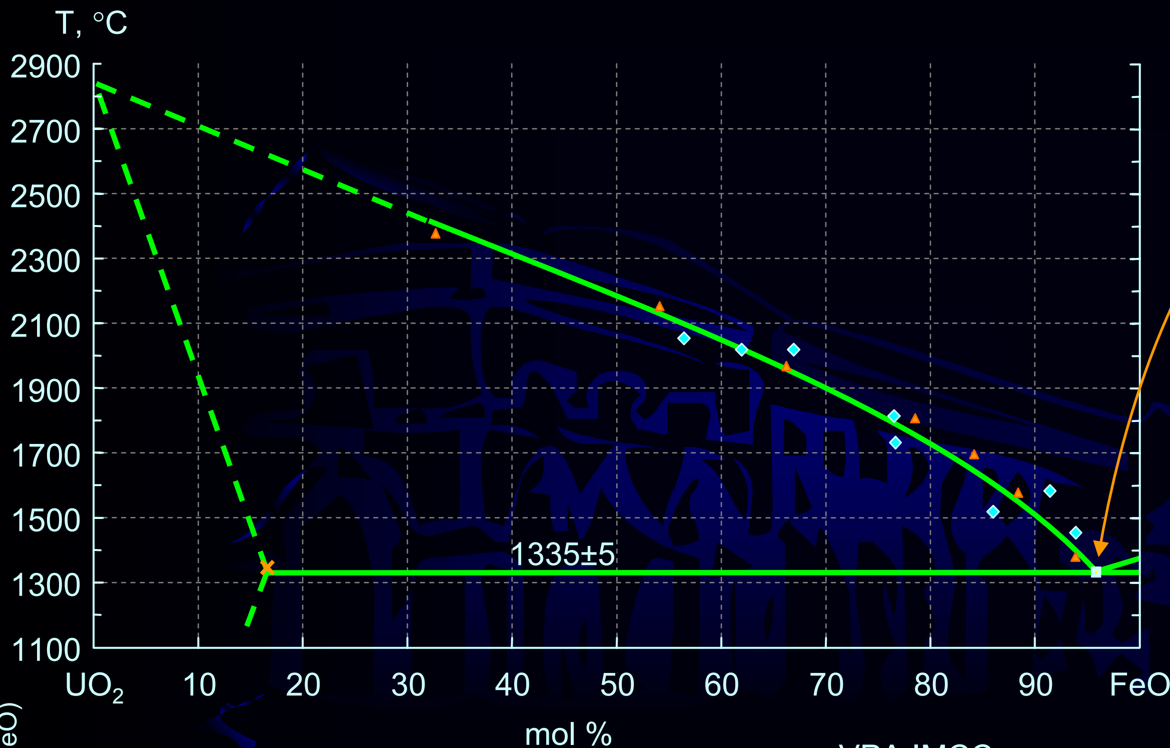


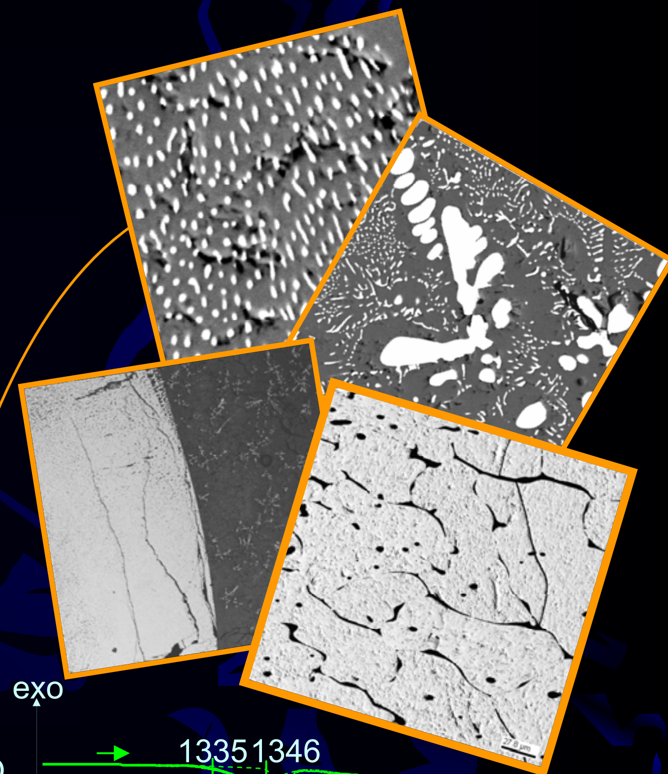
1. Control and monitoring system
2. Pyrometer RAYTEK MR1-SC
3. Video cameras
4. Heater (W)
5. Crucible (Mo)
6. Holder (Mo)
7. Water-cooled furnace wall
8. Electromagnetic lock
9. Chamber for specimen quenching
10. Generator
11. Vacuum pump
12. Gas tank (Ar, Ar+H2, He+ H2)

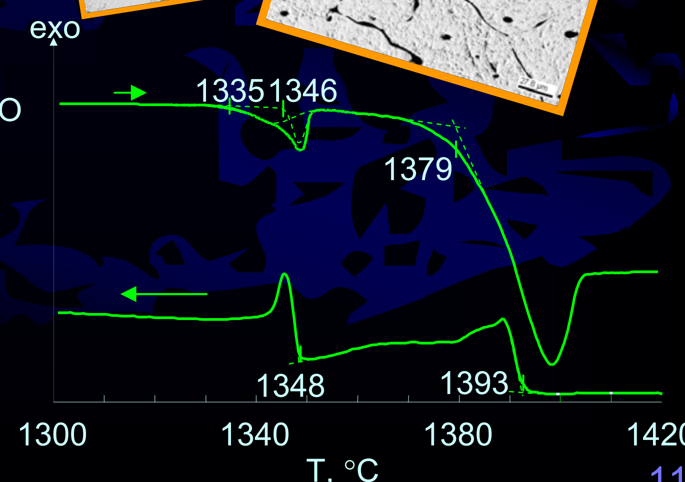
- ✓**Crucible – Mo, Ir, Ta, W, ZrO_2, Al_2O_3, UO_2**
- ✓**Experimental conditions should exclude specimen - crucible interaction**

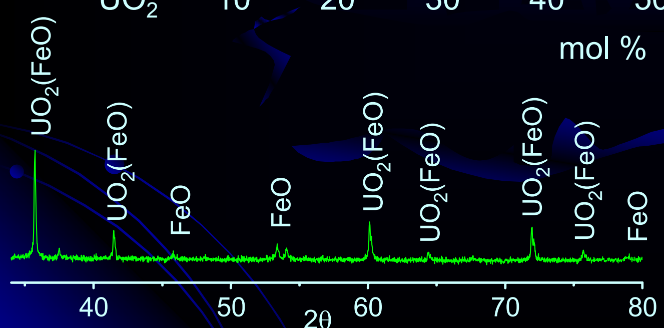
Results: Binary oxide systems

UO_2-FeO



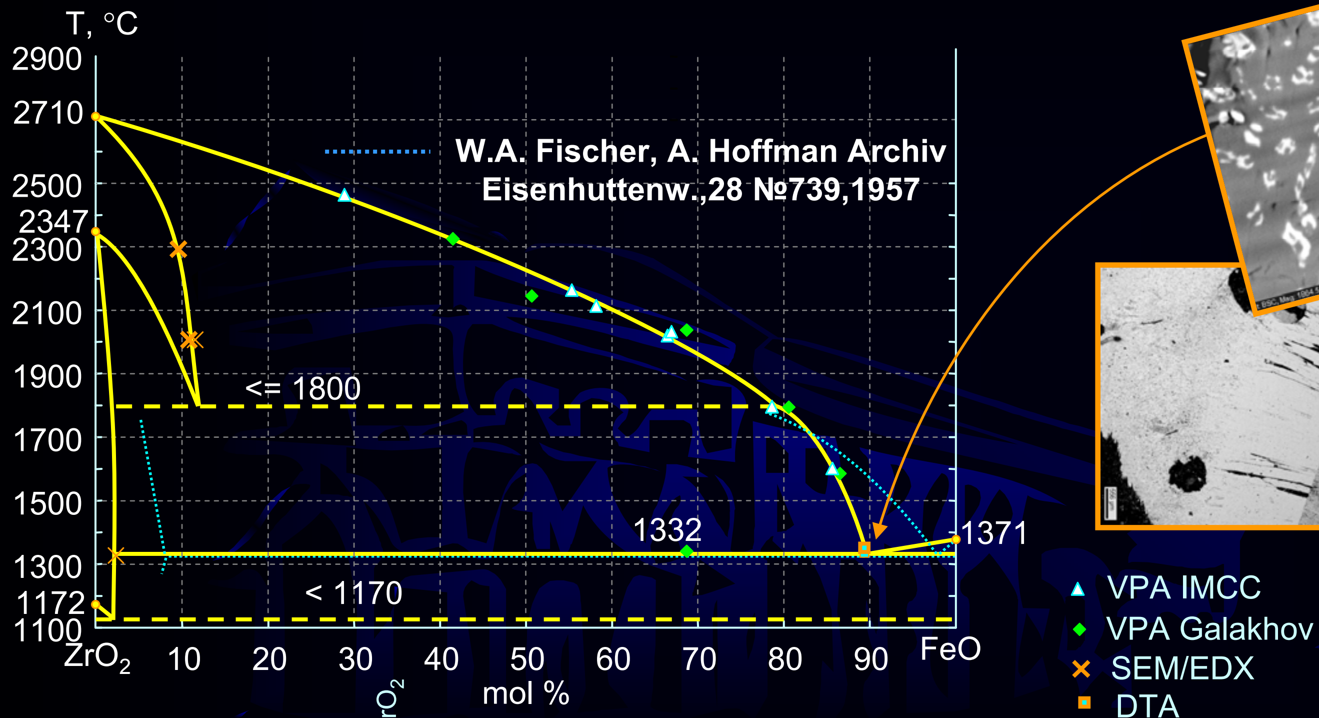


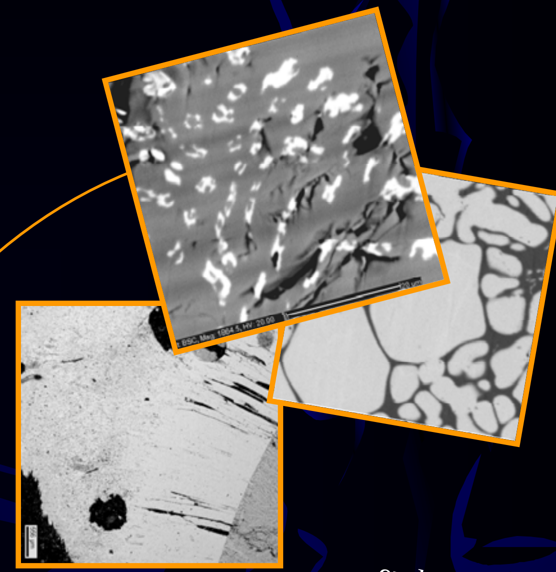


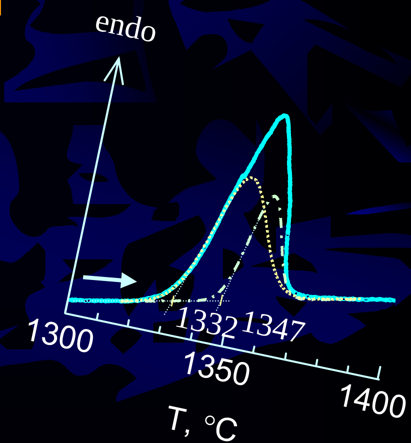


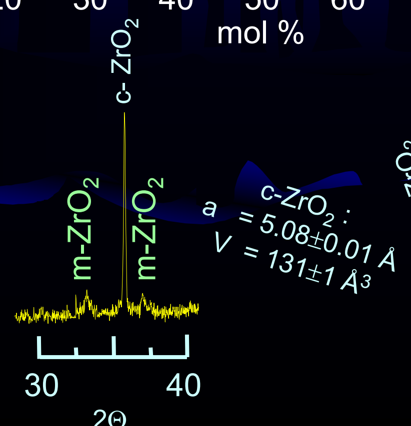
Results: Binary oxide systems

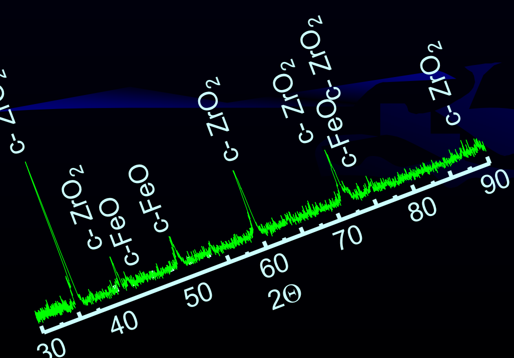
ZrO_2-FeO





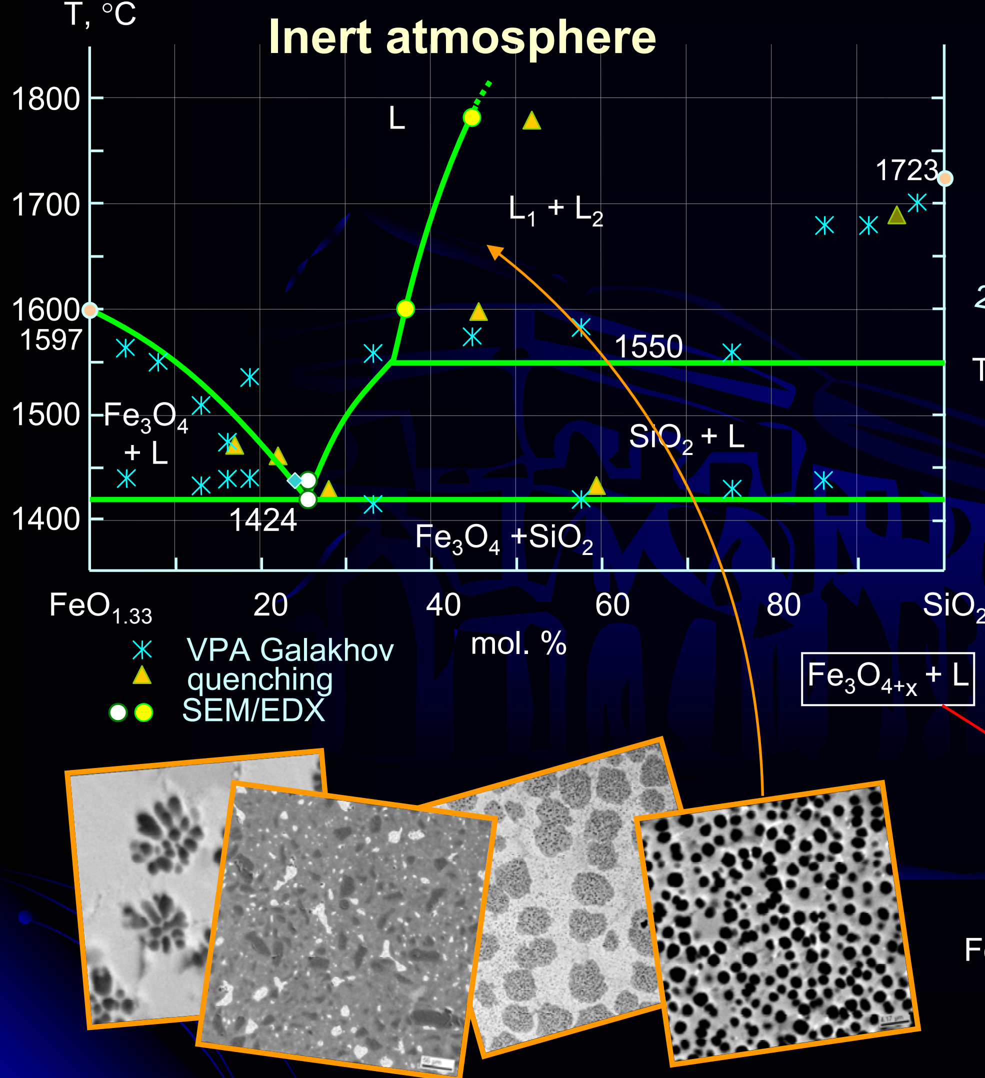


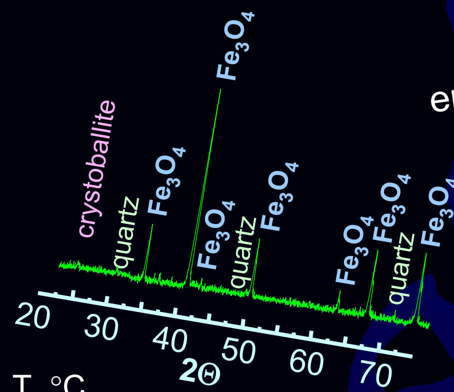


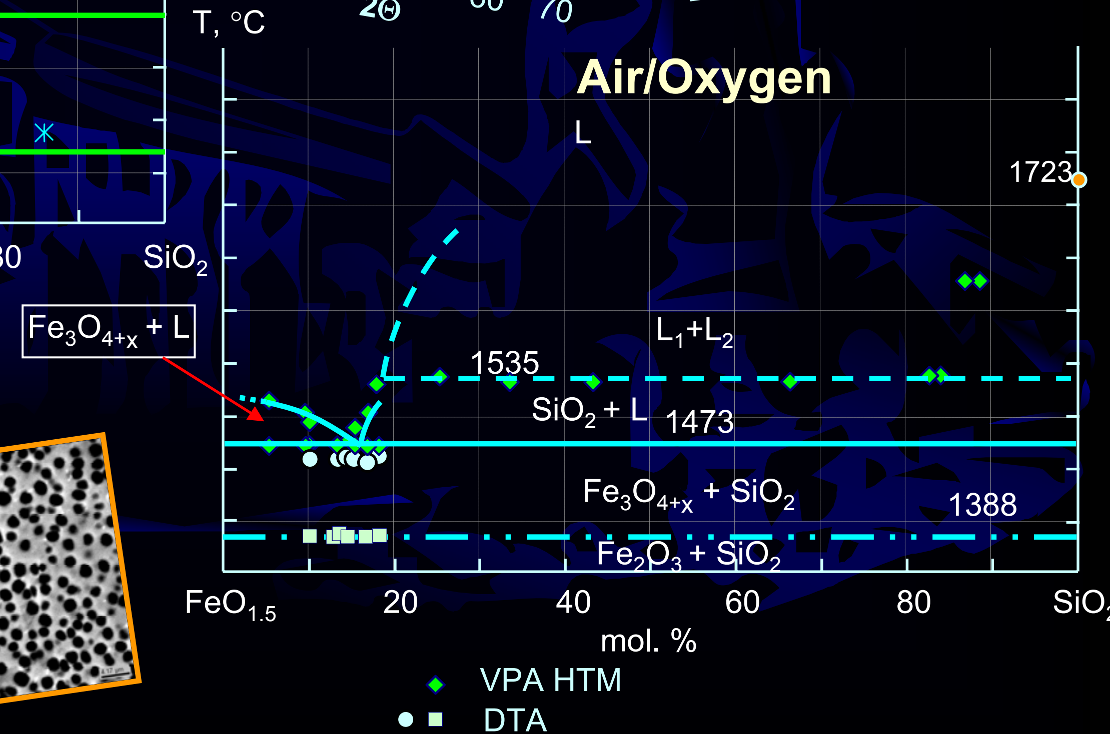


Results: Binary oxide systems

SiO_2- Fe_2O_3/Fe_3O_4

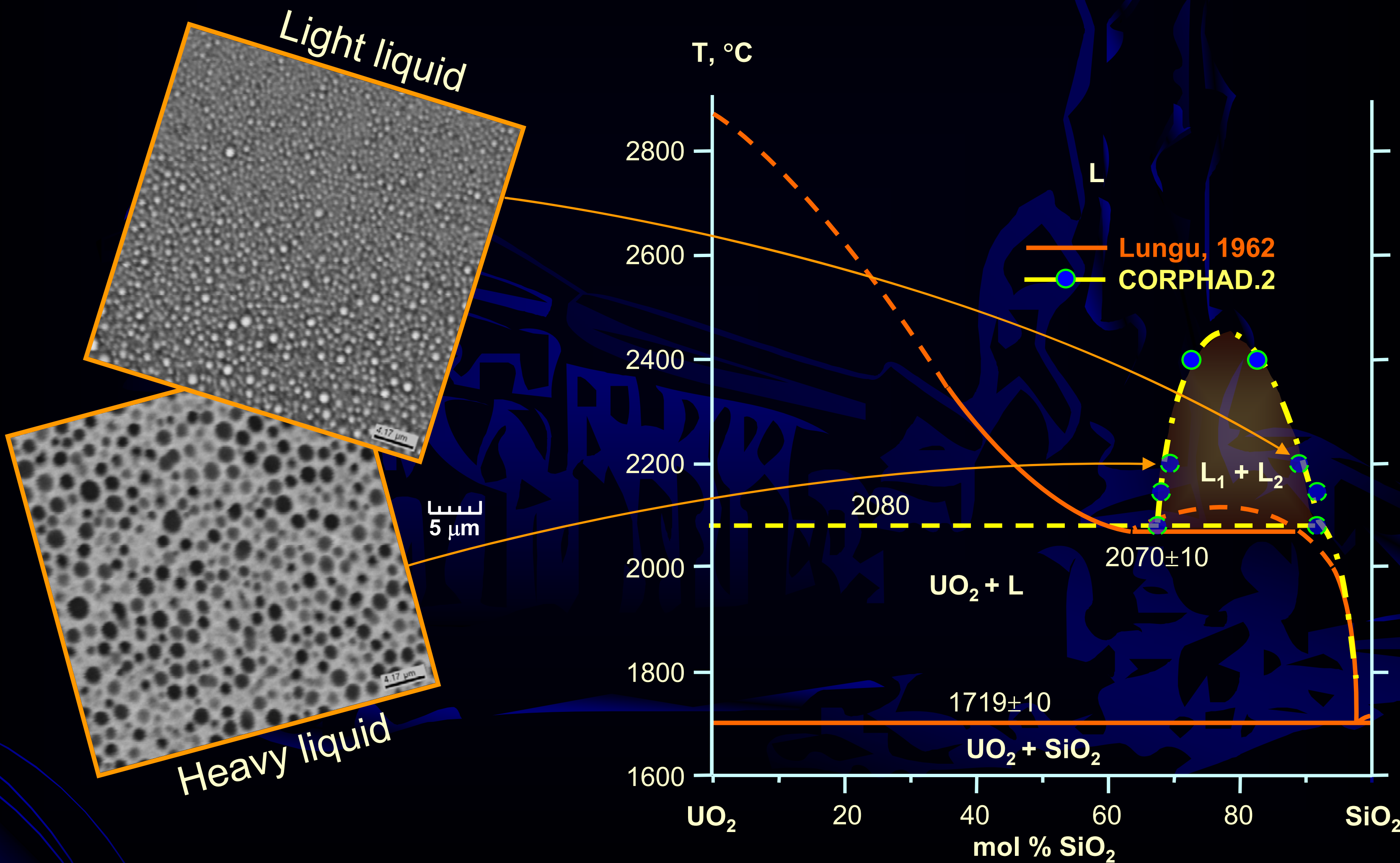






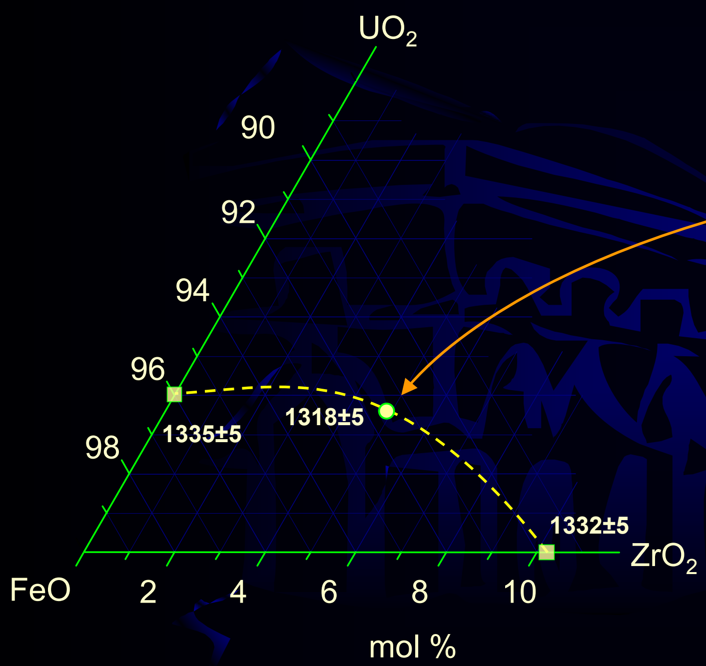
Results: Binary oxide systems

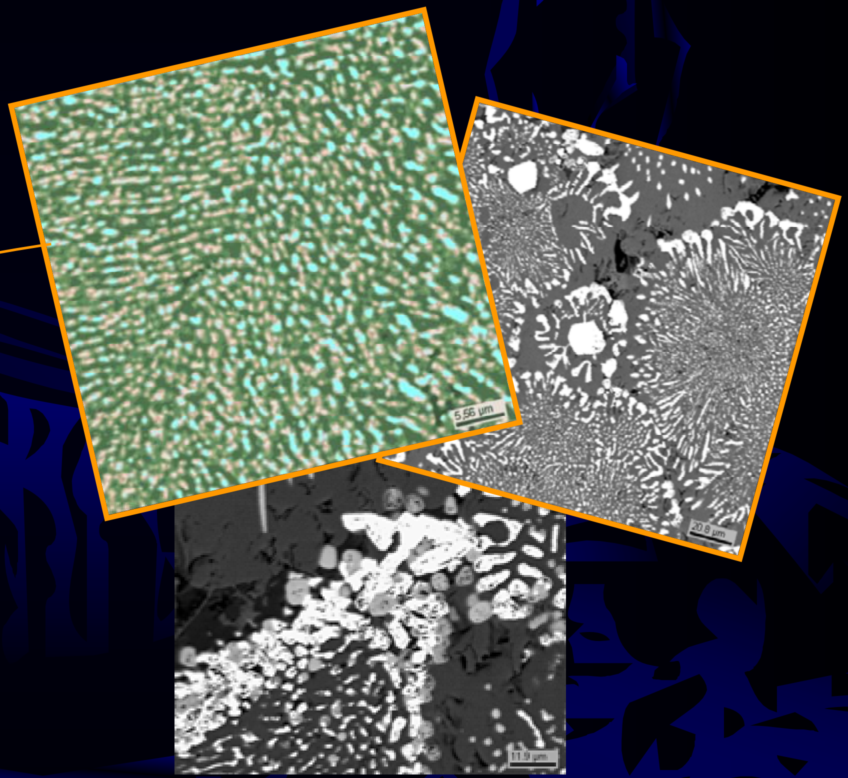
UO_2-SiO_2



Ternary oxide systems

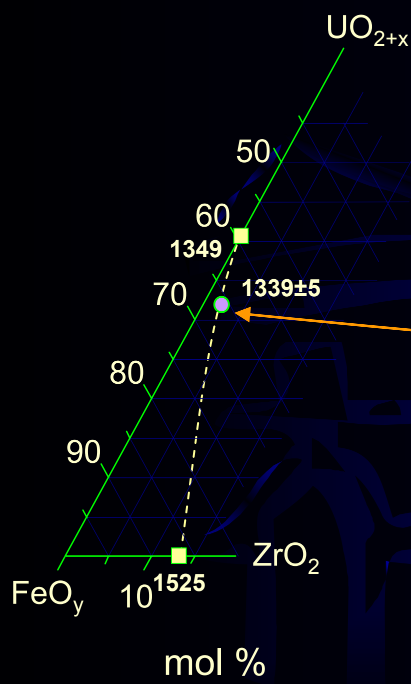
Eutectic point for UO_2-ZrO_2-FeO (argon)

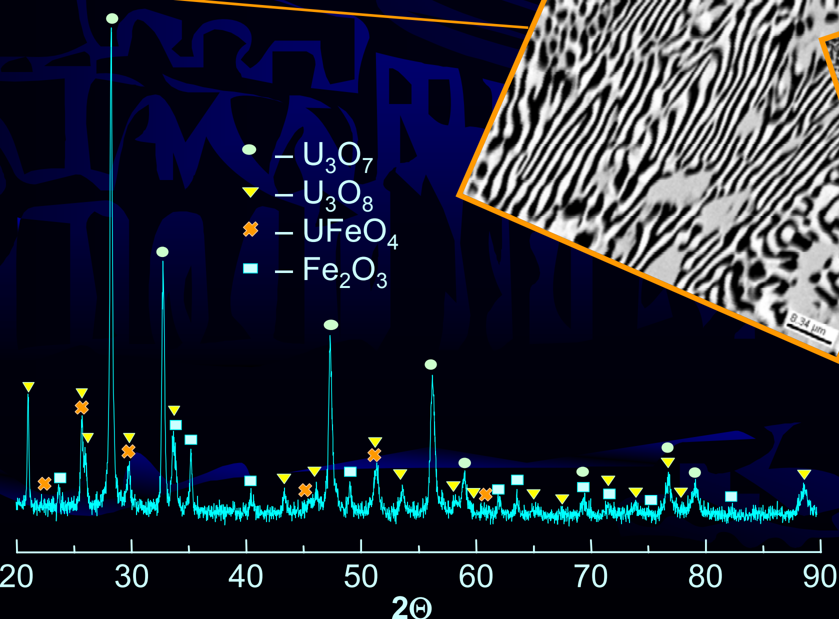


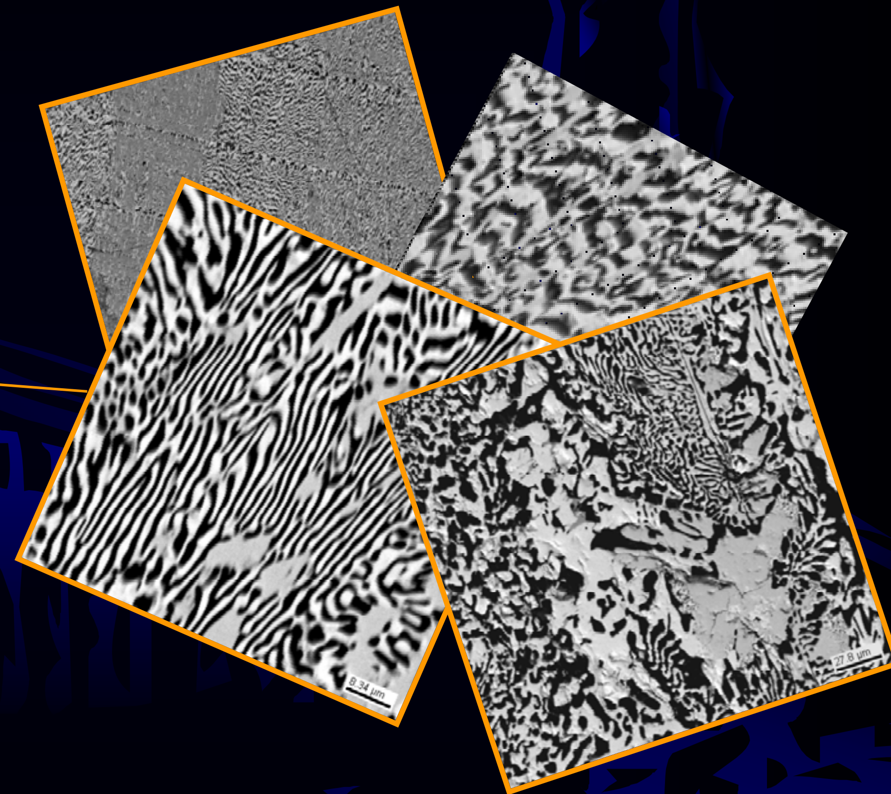


Results: Ternary oxide systems

Eutectic point for UO_2-ZrO_2-Fe_2O_3 (air)

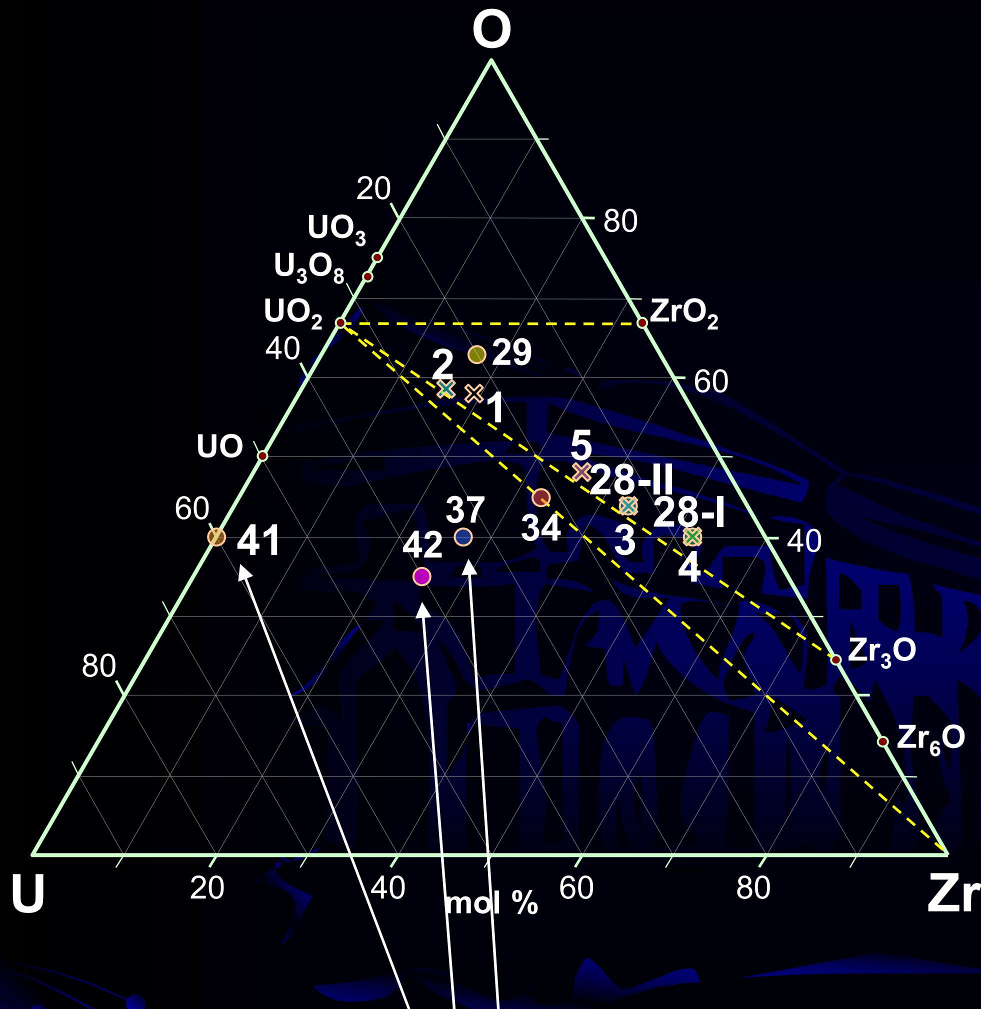






Results: Metal-oxide systems

Liquidus in U-Zr-O



Test	Composition, ат.%			T_{liq}, K	
	U	Zr	O	Test	Calculation
CORD 28-I	7.7	53.7	38.6	2358±35	2238
CORD 28-II	12.9	43.9	43.2	2443±36	2357
CORD 29	19.8	17.2	63.0	2734±41	2803
CORD 34	21.5	34.7	43.8	2578±38	2470
CORD 37	32.5	29.2	38.3	2601±39	2570
CORD 41	56.0	3.1	40.9	2788±42	2690
CORD 42	40.5	27.0	32.5	2663±40	2595
CD-1	22.9	19.1	58.0	2643±39	2650
CD-2	25.7	15.8	58.5	2673±40	2700
CD-3	13.0	43.0	44.0	2408±36	2362
CD-4	8.0	52.0	40.0	2373±35	2231
CD-5	16.0	36.0	48.0	2498±37	2426

Liquid immiscibility was detected

● - CORD series (“Rasplav-3”, Alexandrov RIT)

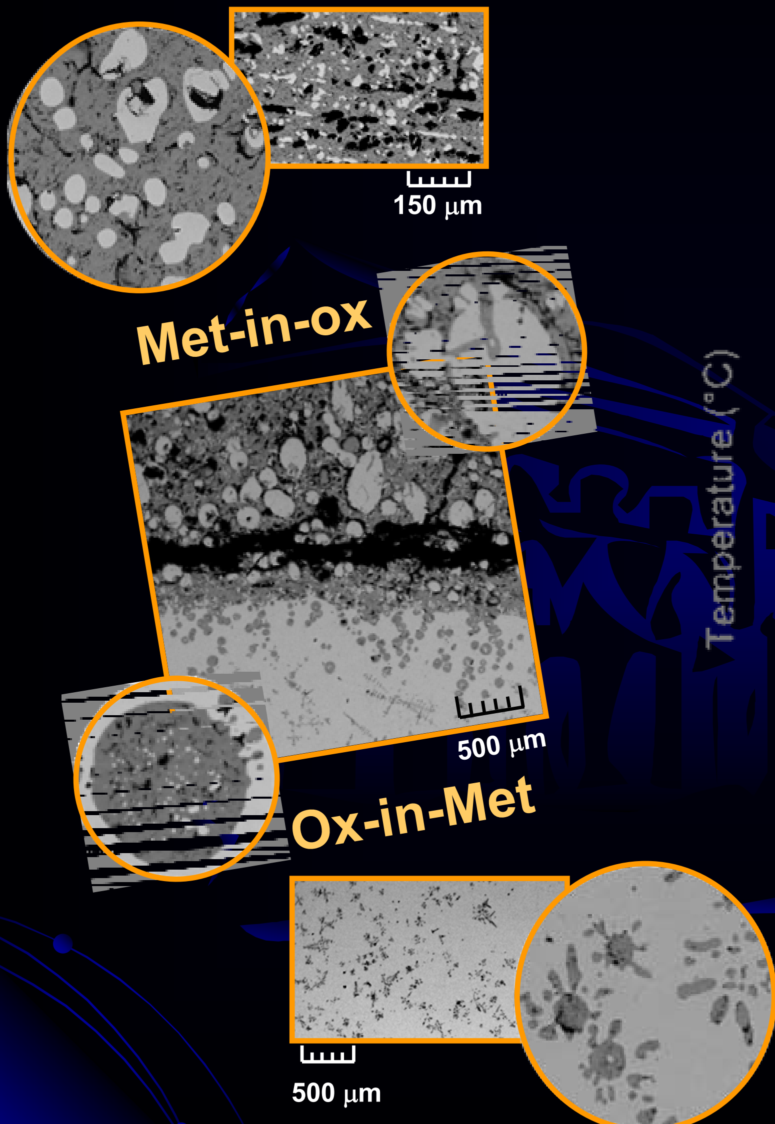
✖ - CD series (“Tigel”, RRC “Kurchatov Institute”)

Solidus data are unreliable

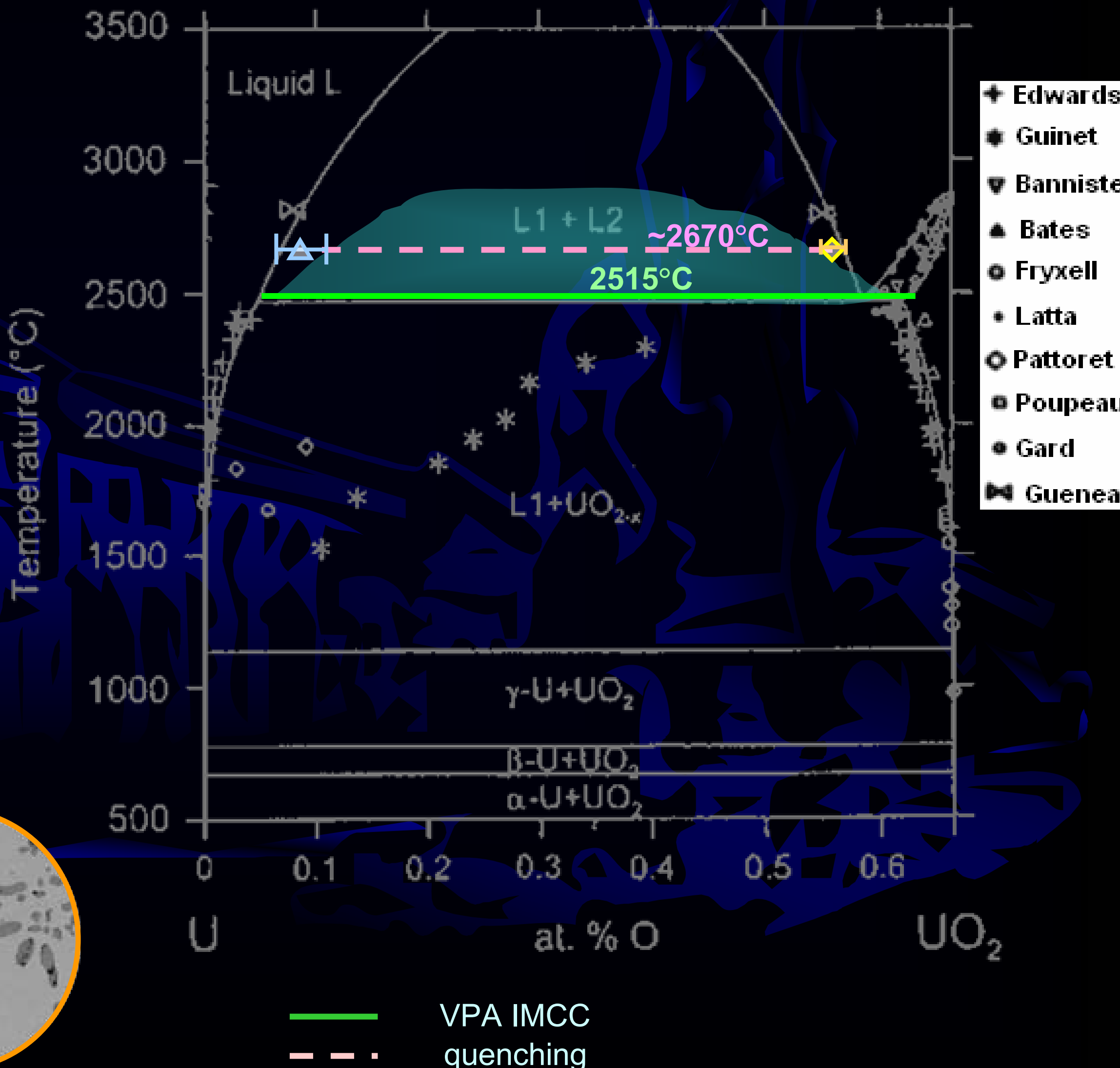
Results: Metal-oxide systems

Methodological test in U-O system

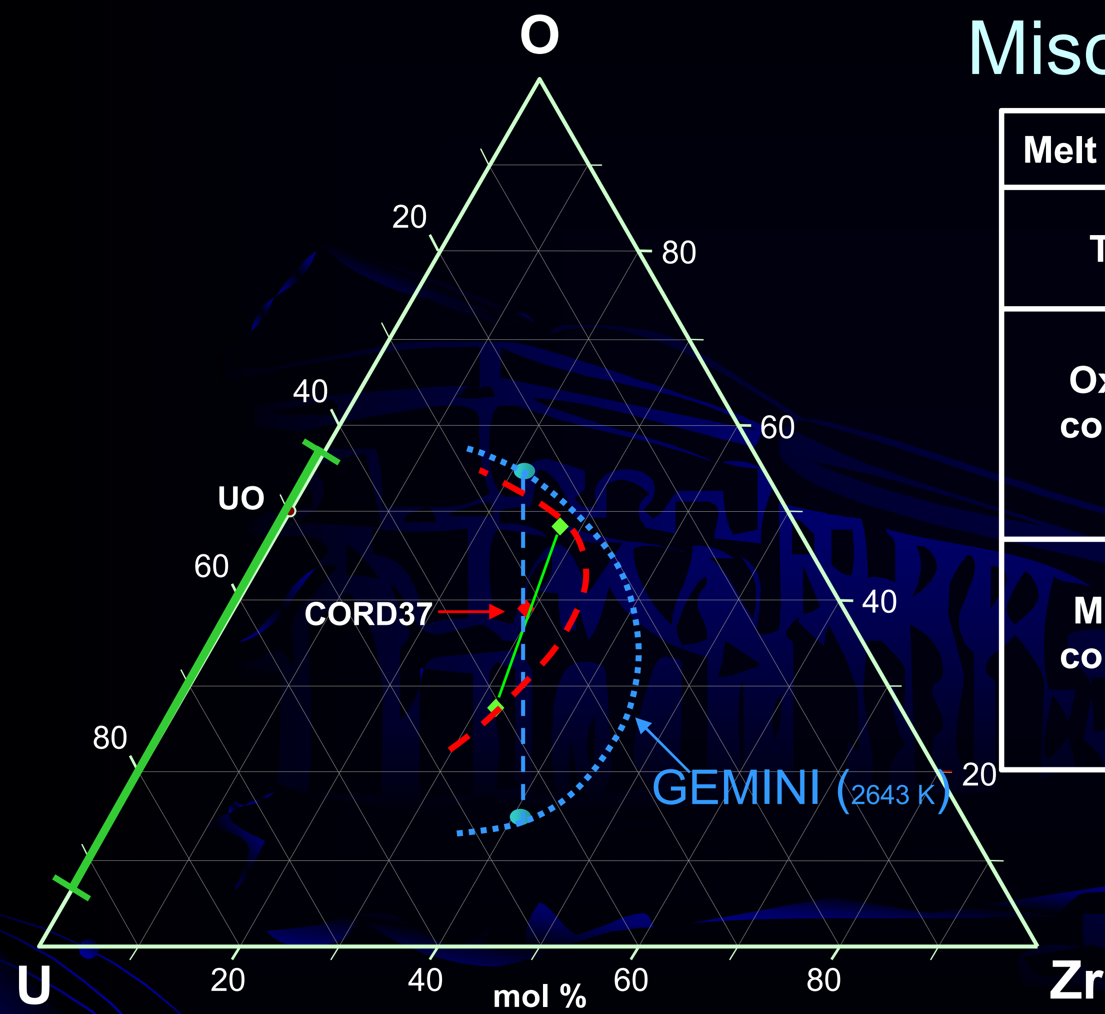
Light liquid



Heavy liquid



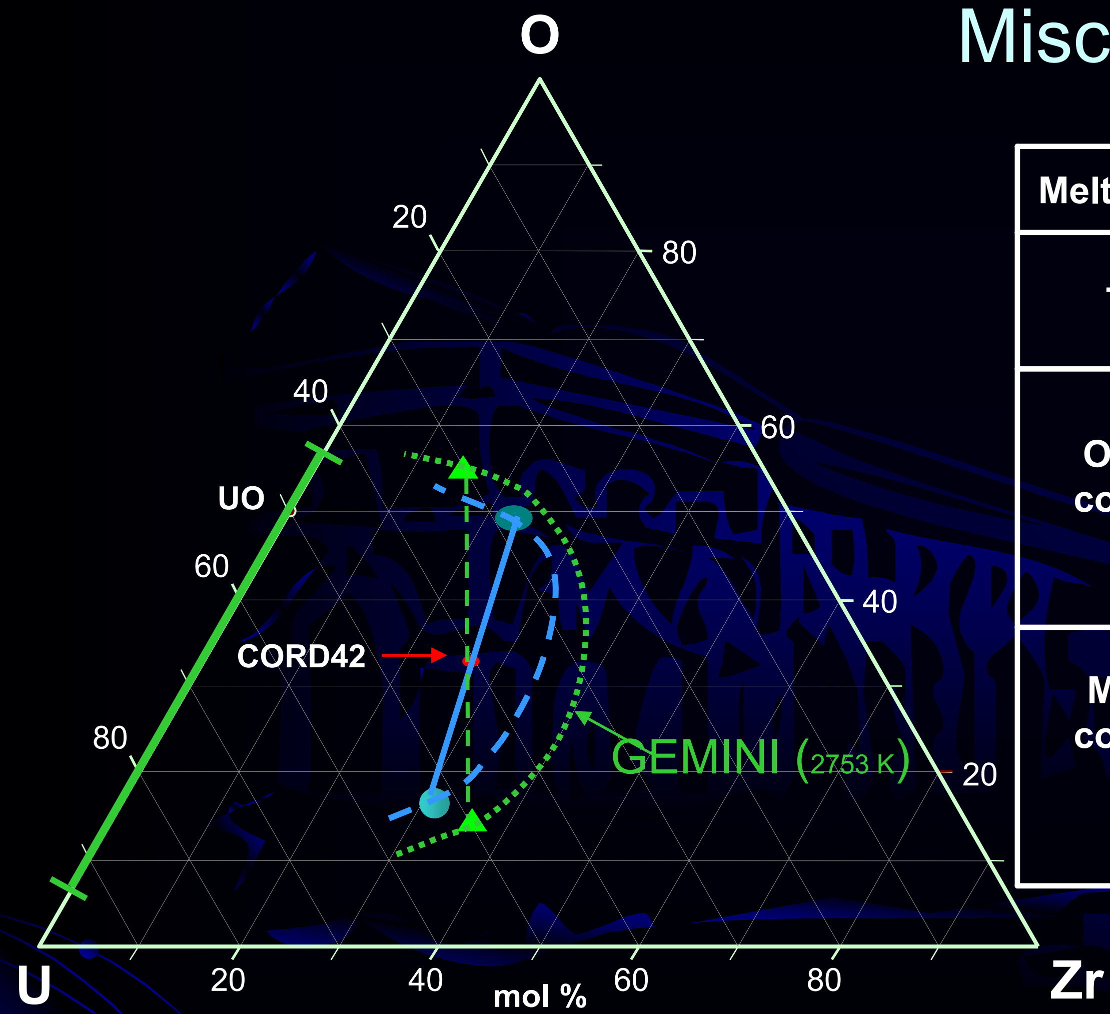
Results: Metal-oxide systems



Miscibility gap in U-Zr-O

Melt composition, ат%		$U_{0.325}Zr_{0.292}O_{0.383}$
Temperature,K		2643
Oxide liquid composition, ат%	U	25.2±1.2
	Zr	26.7±1.3
	O	48.2±2.4
Metal liquid composition, ат%	U	40.8±2.0
	Zr	32.2±1.6
	O	27.2±1.3

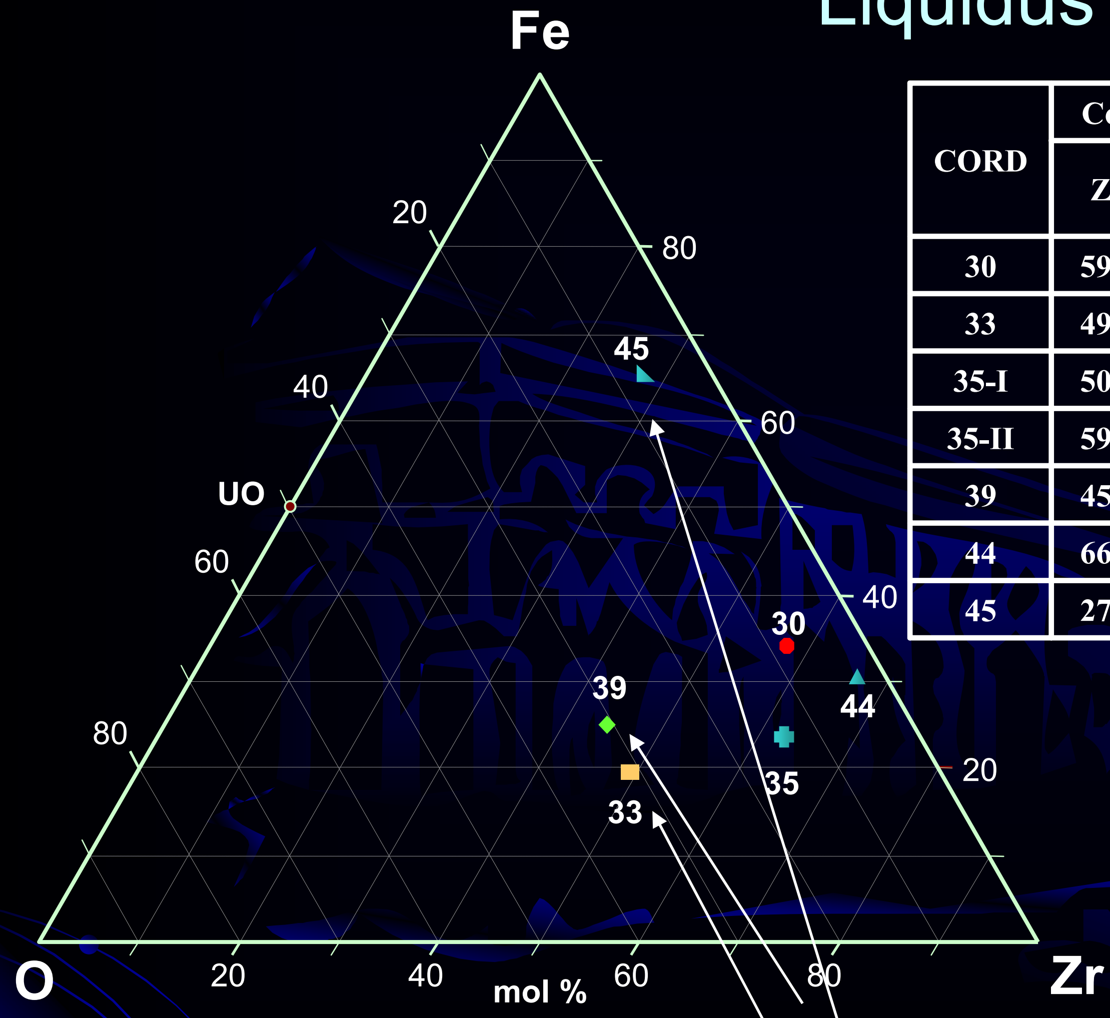
Results: Metal-oxide systems



Miscibility gap in U-Zr-O

Melt composition, aт%		$U_{0.405}Zr_{0.270}O_{0.325}$
Temperature,K		2753
Oxide liquid composition, aт%	U	27.7±1.3
	Zr	23.2±1.1
	O	49.2±2.4
Metal liquid composition, aт%	U	53.2±2.6
	Zr	29.3±1.4
	O	17.6±0.8

Results: Metal-oxide systems



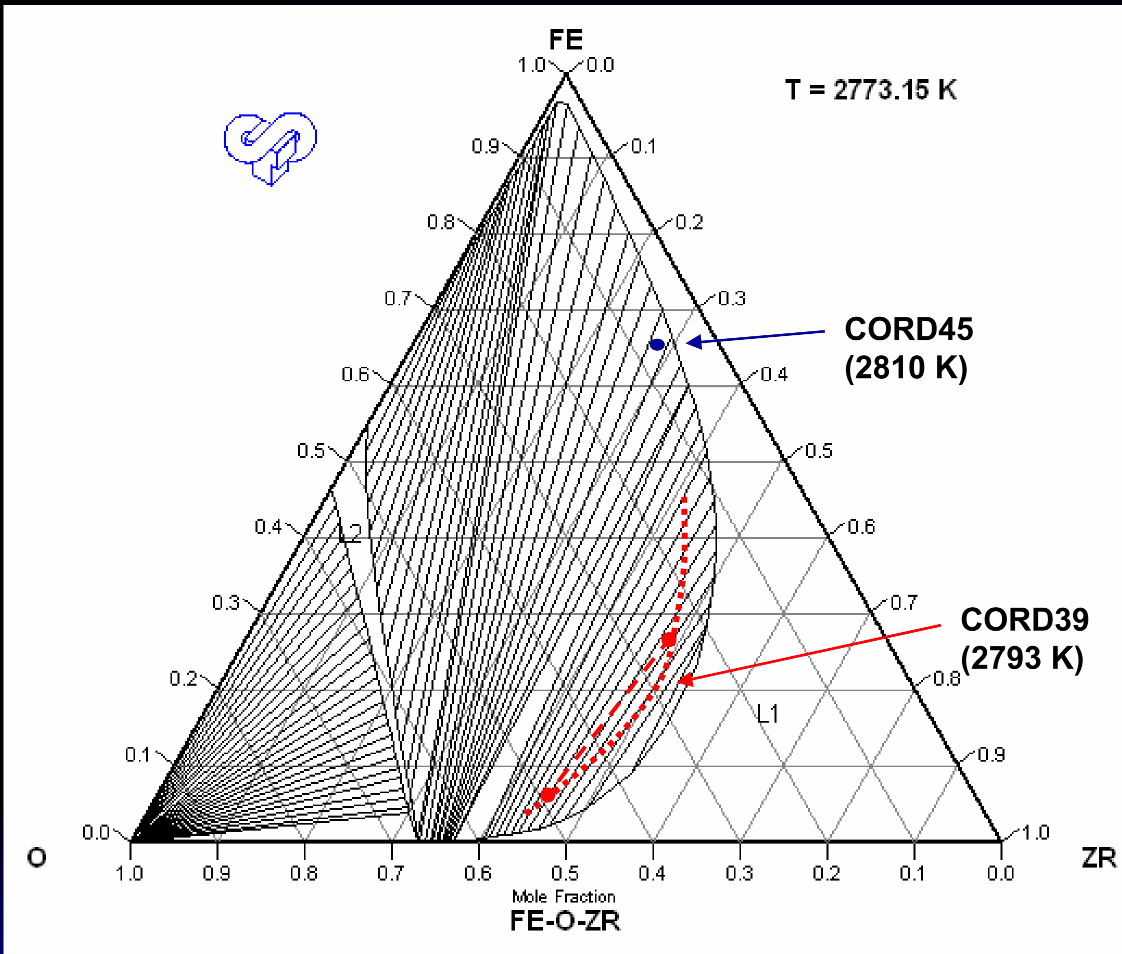
Liquidus and solidus in Zr-Fe-O

CORD	Concentration, at.%			Experiment		Calculation	
	Zr	Fe	O	T_{liq}, K	T_{sol}, K	T_{liq}, K	T_{sol}, K
30	59.1	32.8	8.1	2125	-	2190	1255
33	49.7	19.7	30.6	2655	1707	2622	1750
35-I	50.2	20.0	29.8	2653	1717	2627	1750
35-II	59.2	28.5	12.2	2293	-	2303	1380
39	45.4	25.8	28.8	2763	-	2674	1750
44	66.2	30.7	3.1	2053	1713	2032	1210
45	27.0	65.3	7.7	2793	1796	2820	1610

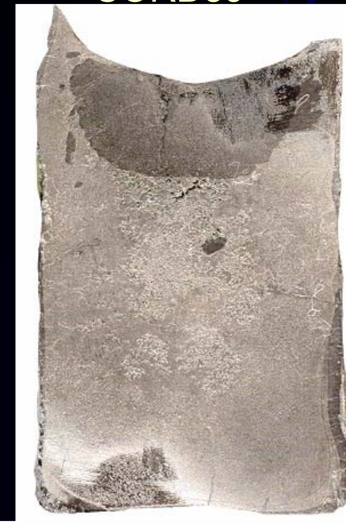
Liquid immiscibility was detected

Results: Metal-oxide systems

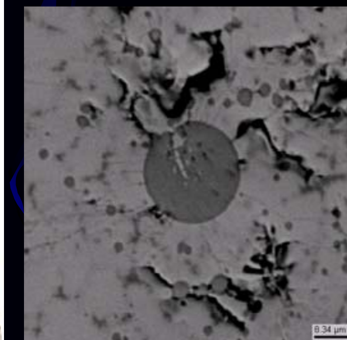
Miscibility gap in Zr-Fe-O



CORD39



CORD45



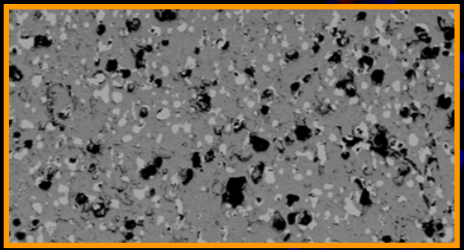
Melt composition, aт%		$Zr_{0.454}Fe_{0.258}O_{0.288}$
Temperature,K		2793
Oxide liquid composition, aт%	Zr	44.8±2.2
	Fe	6.4±0.3
	O	48.7±2.4
Metal liquid composition, aт%	Zr	48.7±2.4
	Fe	26.1±1.3
	O	25.2±1.3

Results: Metal-oxide systems

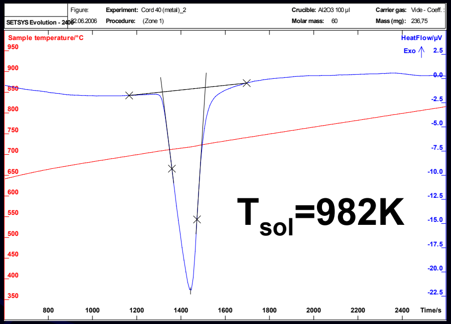
U-Fe-O

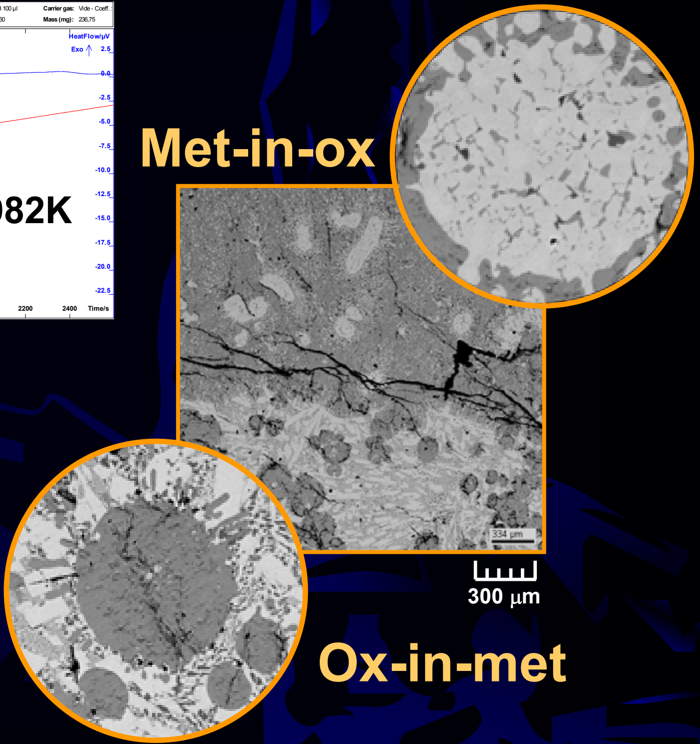
Melt composition, aт%		$U_{0.63}Fe_{0.22}O_{0.15}$
Temperature, K		2873
Oxide liquid composition aт%	U	43.3±2.0
	Fe	2.0±0.2
	O	54.7±3.0
Metal liquid composition aт%	U	68.0±3.0
	Fe	23.5±1.2
	O	8.5±0.8

Light liquid

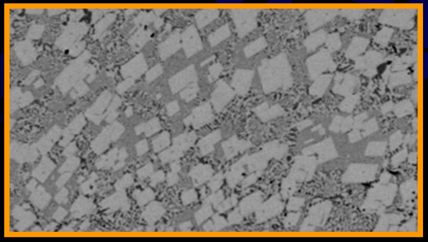


150 µm



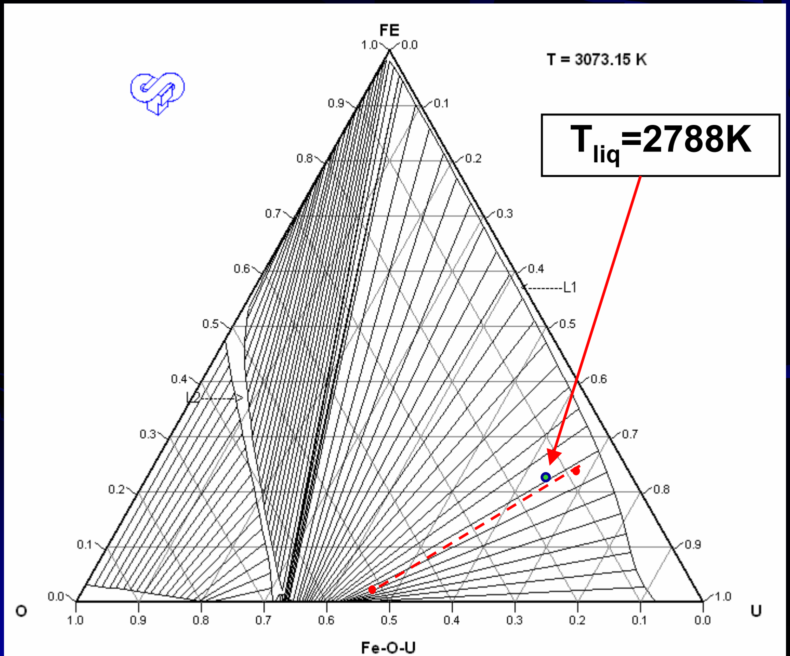


300 µm



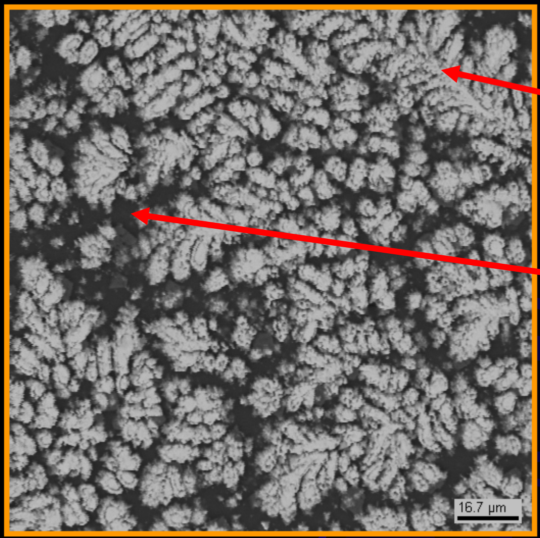
80 µm

Heavy liquid



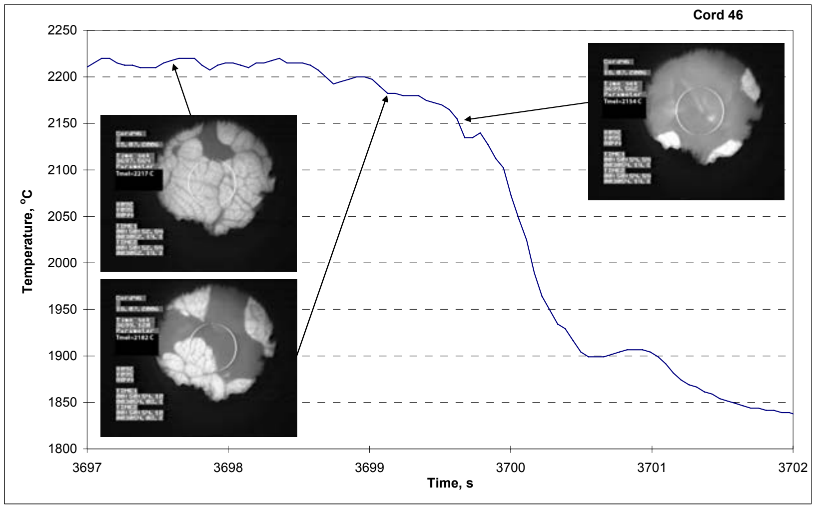
Results: Complex corium mixture

$54.2UO_2 – 13.7SiO_2 – 17.9ZrO_2 – 1.3Al_2O_3 – 3.8CaO – 7.6FeO – 1.5Cr_2O_3$



(UZr(Si,Fe,Ca,Al))O

(SiCaFeAl(U,Zr))O



Melt composition, mass%	UO_2	ZrO_2	FeO	SiO_2	CaO	Al_2O_3	Cr_2O_3	Experimental data		Calculation	
								T_{liq}, K	T_{sol}, K	T_{liq}, K	T_{sol}, K
	53.0	18.6	7.8	12.9	3.8	2.0	1.9	2493	1477	2290	1350

CORPHAD Reports

Report code	Title	Status
RCP-0401	Investigation of binary oxidic systems: System UO_2-FeO	Done
RCP-0402	Investigation of binary oxidic systems: System ZrO_2-FeO	
RCP-0403	Phase relation study in the system $Fe_2O_3(Fe_3O_4) – SiO_2$ at different oxygen partial pressures	
1-1950.2-2004	PROJECT № 1950.2. Annual progress report. First year	
RCP-0404	Investigation of ternary oxidic systems: UO_x-ZrO_2-FeO_y	
2-1950.2-2005	PROJECT № 1950.2. Annual progress report. Second year	
Z 1.5-1950.2r	Investigation of ternary metal/oxide systems: U-O-Zr	Russian version
Z 1.6-1950.2r	Investigation of ternary metal/oxide systems: Zr-O-Fe	
Z 1.7-1950.2r	Investigation of ternary metal/oxide systems: U-Fe-O	
Z 1.8-1950.2r	Investigation of oxidic systems:UO_2-SiO_2	
Z 1.9-1950.2r	Investigation of complex corium mixrure	

CORPHAD Papers

Bechta S.V., Krushinov E.V., Almjashev V.I., Vitol S.A., Mezentseva L.P., Petrov Yu.B., Lopukh D.B., Khabensky V.B., Barrachin M., Hellmann S., Froment K., Fischer M., Tromm W., Bottomley D., Defoort F., Gusarov V.V. **Phase diagram of the ZrO_2–FeO system** // J. Nucl. Mater. Vol. 348, pp. 114-121 (2006)

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CORPHAD Papers in preparation

Draft titles:

Eutectic compositions in the UO_2–ZrO_2–FeO/Fe_2O_3 systems

Miscibility gap in the UO_2–SiO_2 system

Miscibility gap in the U–O system

CORPHAD-P * Matrix

Task	Composition	Atmosphere	Experimental data	Priority level	Pt N
1	Different compositions in the U-Zr-Fe-O system	Argon	Selected points (liquidus, solidus, tie-lines in the miscibility gap)	1	3
2	ZrO_2 - FeO_y	Air and p_{O_2} control	liquidus, solidus, solubility limits	2	3
	UO_2 - SiO_2	Argon	liquidus, solidus, solubility limits, eutectic point	1	7
	CaO - UO_2			1	7
	CaO - FeO			2	3
3	UO_2 – FeO – SiO_2		liquidus, solidus solubility limits, tie-lines in the miscibility gap, ternary eutectic point	1	10
	UO_2 – FeO – CaO		liquidus, solidus solubility limits, ternary eutectic point	1	10
	ZrO_2 - FeO - SiO_2		ternary eutectic point	2	2
	ZrO_2 - FeO - CaO		ternary eutectic point	2	2
4	Realistic complex corium mixture	Argon or Air	Eutectic composition measurement proposed by French partners (1 system), proposed by German partners (1 system), proposed by Russian partners (1 system)	2	3

***) - tentative title**

Concluding remarks

- ✓CORPHAD data for oxide systems have been finalized, partially published and used for optimization of NUCLEA database
- ✓Data for metal/oxide systems will be finalized after discussion with collaborators at the last project meeting (May 2007, St-Petersburg)
- ✓Technical content of CORPHAD-P project proposal has been agreed about. The proposal will be prepared to the next CEG-SAM