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Progress report on the ISTC project #3813: Phase relation in corium systems (PRECOS)

Presented by S. Bechta
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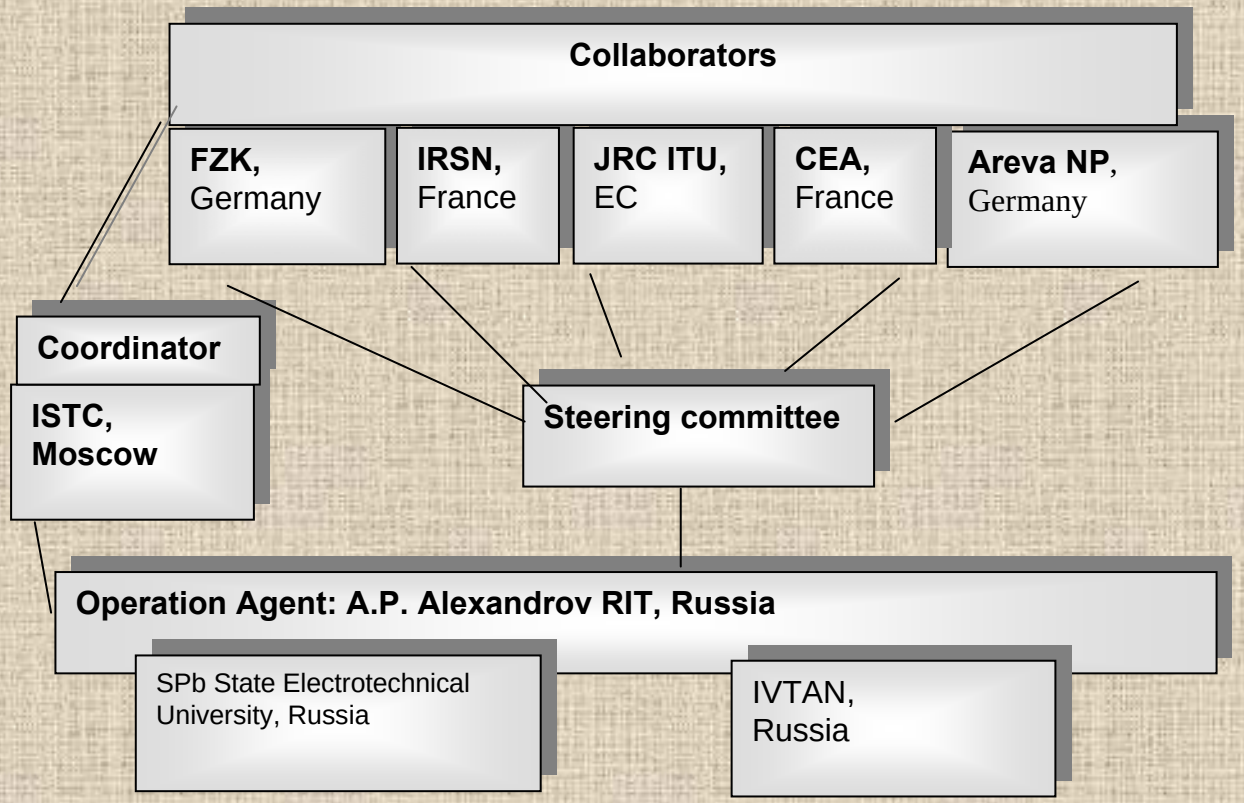
- Conclusions

PRECOS project general information

Project participants and coordination



Project duration	**36 months**
Financial party	**Europe**
Funding	**995,610 USD**
Project status	**In Progress**

Project objectives

Experimental determination of:

- liquidus – solidus temperatures
- coordinates of reference points (eutectics, etc.)
- solubility limits of solid solutions
- compositions of liquids coexisting in the miscibility gap

PRECOS test 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	6
2	ZrO_2 - FeO_y	Air and p_{O_2} control	liquidus, solidus, solubility limits	2	3
	UO_2 - SiO_2	Neutral	liquidus, solidus, solubility limits, eutectic point	1	7
	CaO - UO_2			1	7
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	Eutectic composition measurement of a realistic complex corium mixture	Argon or Air	System (atmosphere) proposed by: - French partners (1 system) - German partners (1 system) - Russian partners (1 system)	2	3

Scope of work in quarters 6-7

- ✓ The laser pulse heating (LPH) experimental installation at IVTAN is equipped with a system of high-speed video recording of the specimen surface at 1000 frames/s
- ✓ A new system of semi-transparent ceramics heating by the Nd:YAG laser has been designed and realized for the above installation
- ✓ ISC experimental installations have been transferred to SPb SETU and assembled there. Their commissioning and adjustment are underway. The electron microscope is equipped with the BRUKER QUNTAX-200 microanalyzer. The company has solved the software- and hardware-related problems of quantitative analysis
- ✓ Experiments on the following systems have been performed:

  UO_2-SiO_2, UO_2-CaO, UO_2-SiO_2-FeO
- ✓ Experiments on the ZrO_2-FeO_y system are delayed due to the transfer of the experimental installations from ISC to SETU, and those on the ZrO_2- U system – because IVTAN has not got yet a License to work with uranium

Scope of work in quarters 6-7 (2)

System	Test	Objective	Status
UO_2-SiO_2	PRS 9 GPRS 19-28,32	Determination of T_{liq} and MG critical point	Tests done Post test analysis in progress
UO_2-CaO	PRS 10 LPH 2	Determination of: -T_{liq} and T_{sol} - final solubility - CaO melting point	
ZrO_2-FeO-SiO_2	GPRS 33-36	T_{liq}, T_{sol}, solubility limits, tie-lines in the miscibility gap, ternary eutectic point	

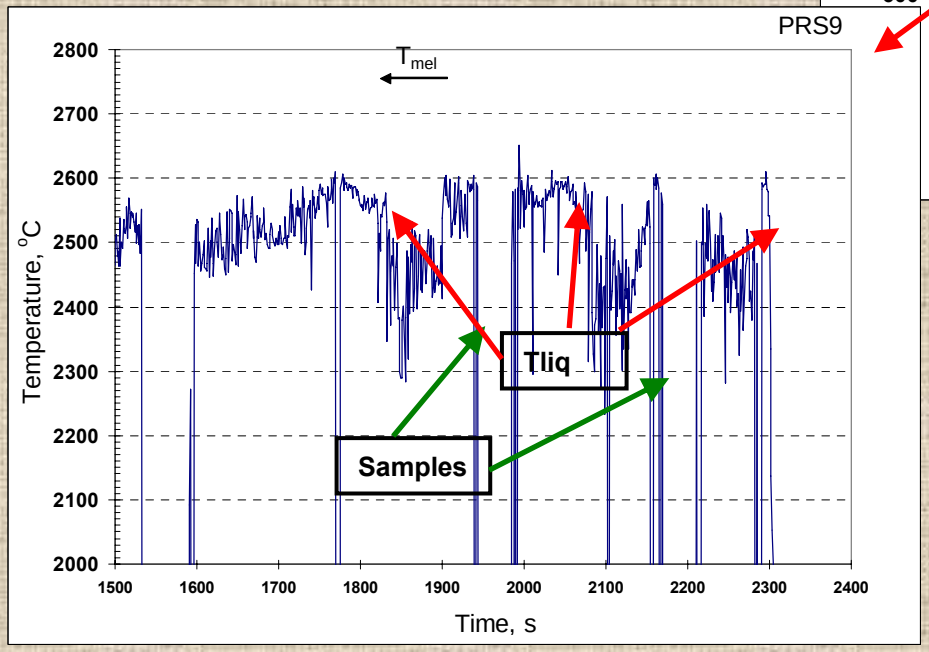
UO_2-SiO_2 system: PRS9 test results

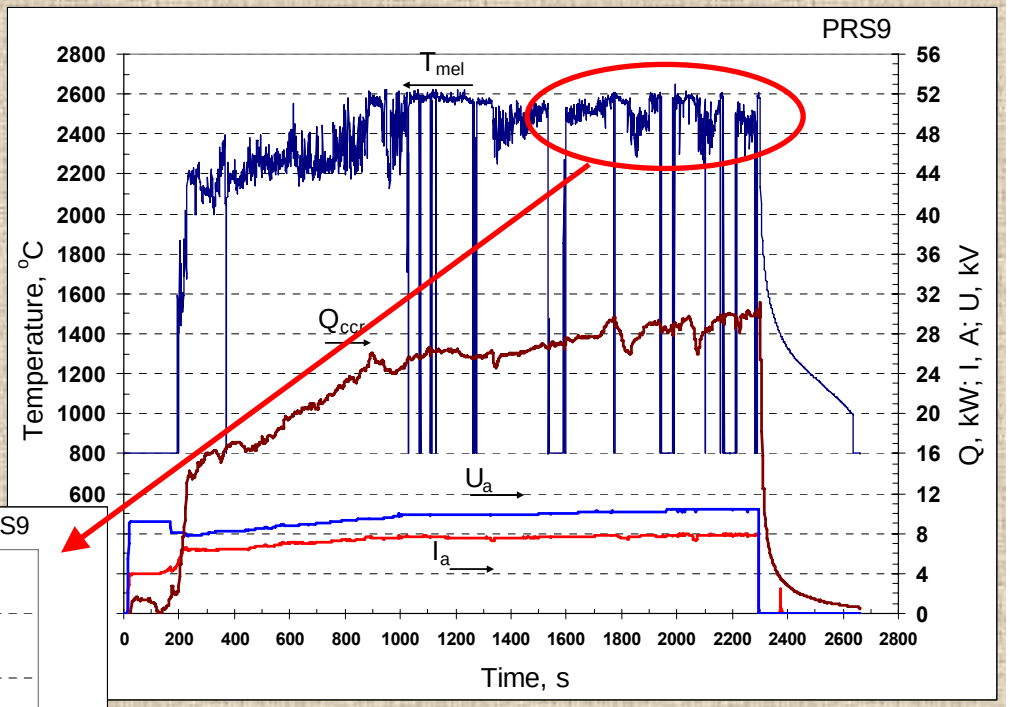
➢Experimental objectives

- Determination of the liquidus temperature

➢Charge composition

- Mol% $75UO_2 + 25SiO_2$

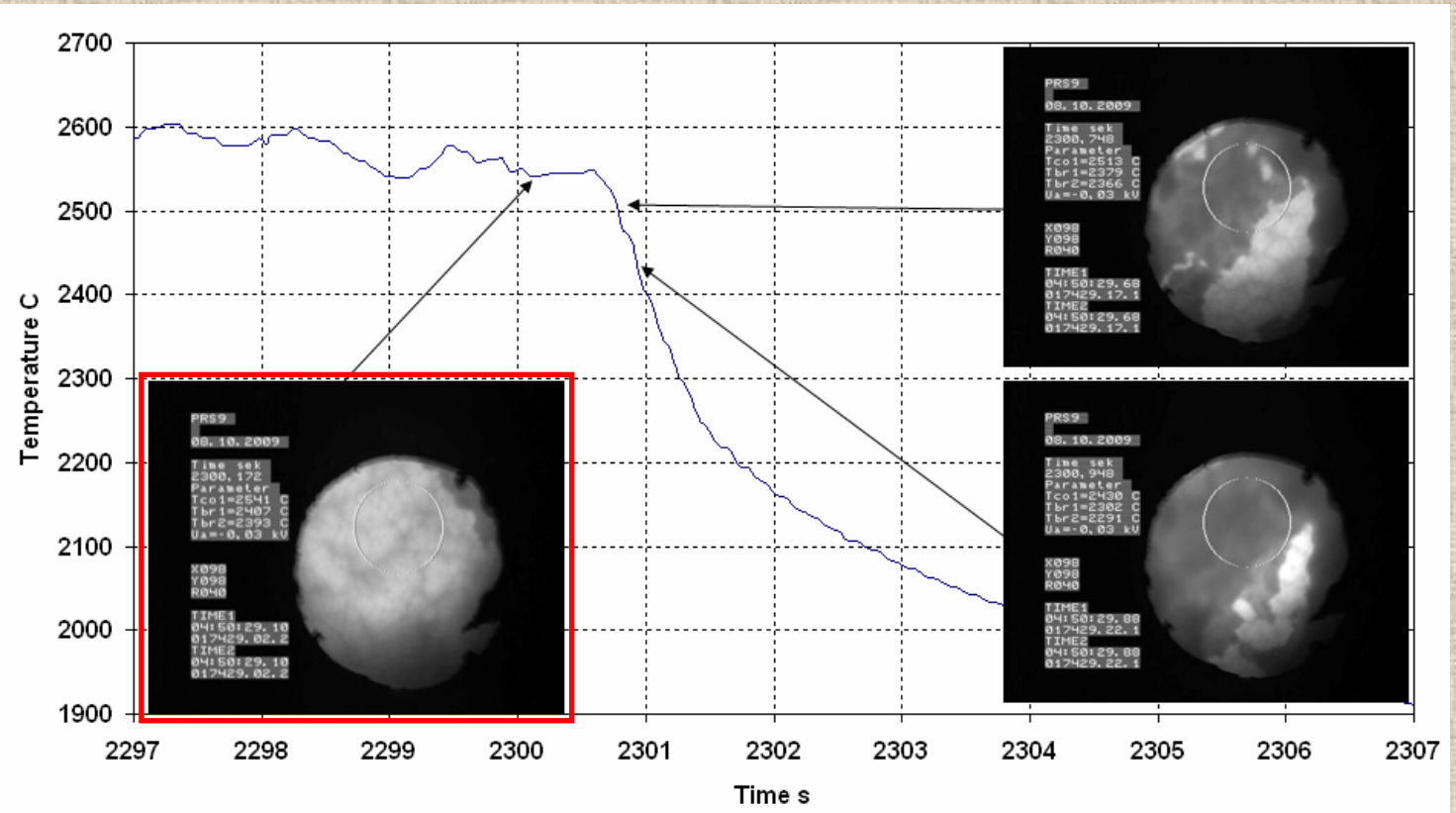




✓ T_{liq} was measured 3 times by VPA IMCC with melt sampling

UO_2-SiO_2 system: PRS9 test results(2)

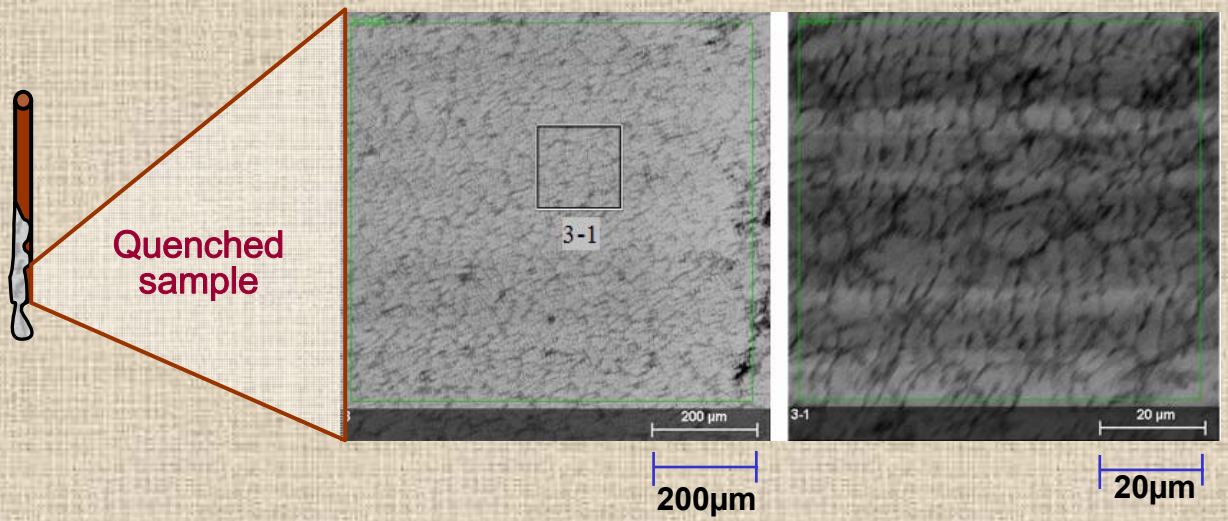
- **VPA IMCC: Example of thermogram # 3 from the test showing melt surface images**



- ✓ Results of T_{liq} measurements: 2560°C, 2563 and 2550°C ⇨ T_{liq}=2558±40°C

UO_2-SiO_2 system: PRS9 test results (2)

- **SEM/EDX of a melt sample**



✓**Dendritic microstructure**

Sample	EDX	ChA
	mol.%UO_2	
№2	73.1	76.7
№3	70.2	77.0

✓**The discrepancies between the EDX and ChA results are being investigated**

UO_2-SiO_2 system: GPRS 19-28,32 test results

- **Experimental objectives**
  - Determination of the critical point of MG cupola
  - Determination of the liquidus point by the lever rule
- **Annealing, melting and quenching in the Galakhov microfurnace**

Test	UO_2 content, mol%	Quenching T,°C	Exposure time, min
GPRS19	70	2200	10
GPRS20	60		
GPRS21	50		
GPRS22	40		
GPRS23	70	2300	
GPRS24	60		
GPRS25	19	2175	
GPRS26	50	2300	
GPRS27	19	2160	
GPRS28	40	2300	
GPRS32	19	2130	

✓UO_2 of >99.0 % purity, SiO_2 of 99.99% purity, charge mass – 150 mg

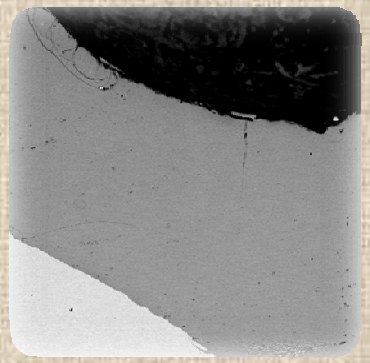
✓SEM/EDX in progress but some results are already available

Critical point experiments (GPRS 18, 25, 27, 32)

Small crucibles, 10 min. exposure in the critical point expected temperature range, quenching

81.4 mol.% SiO_2 by synthesis (the composition is close to the axis passing through the cupola top)

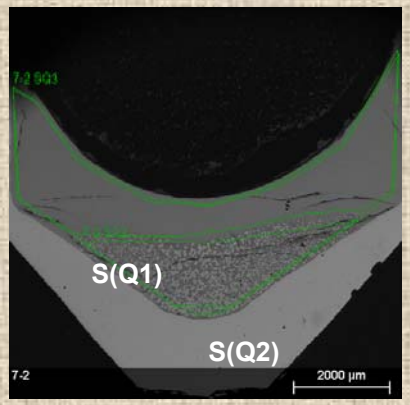
GPRS18



2200 °C

Above the critical point

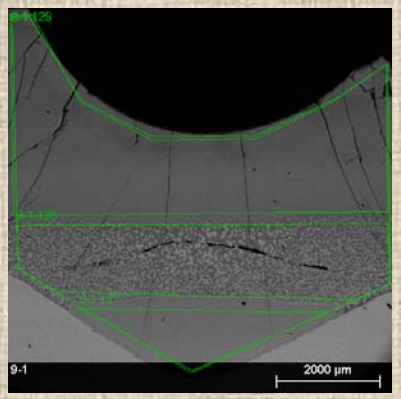
GPRS25



2175 °C

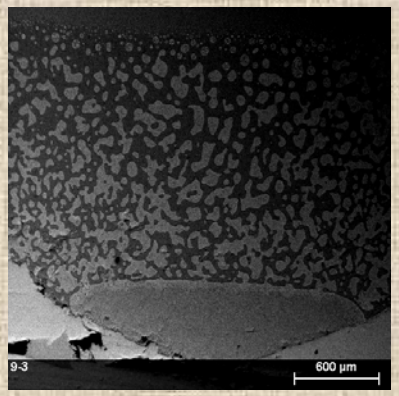
Below the critical point

GPRS27

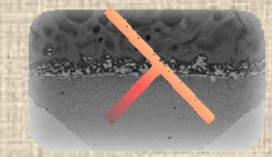


2160 °C

GPRS32



2130 °C



GCORD4, 81.4 mol.% SiO_2
1 min., 2200 °C

	UO_2	SiO_2
	mol.%	
S(Q1)	18.6	81.4
S(Q2)	21.3	78.7

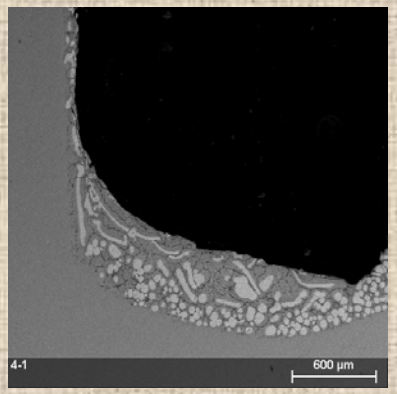
✓Compositions of the upper and lower liquids are close to each other

✓The results indicate critical point between 2200 and 2175°C

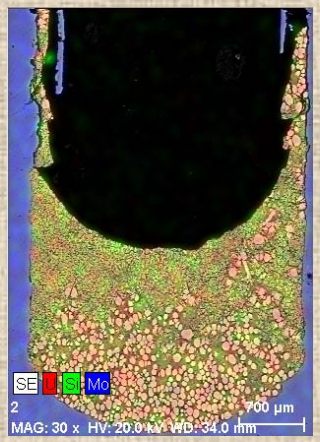
Liquidus experiments (GPRS 19-22)

10 min. exposure, quenching, T= 2200°C

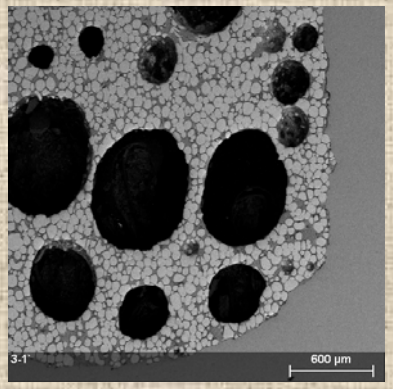
GPRS22



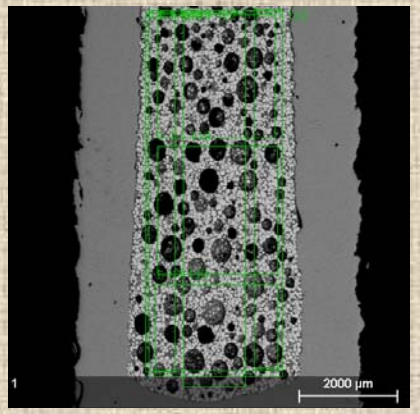
GPRS21



GPRS20



GPRS19

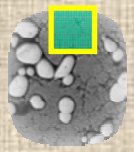


60 mol.% SiO_2 by synthesis

50 mol.% SiO_2 by synthesis

40 mol.% SiO_2 by synthesis

30 mol.% SiO_2 by synthesis



Liquid phase composition measurements

60.5 mol.% SiO_2

66.3 mol.% SiO_2

64.4 mol.% SiO_2

61.4 mol.% SiO_2

- ✓ **A solid relict phase has been registered at the 2200°C isotherm in all samples**

Liquidus experiments (GPRS 23,24,26,28)

Peculiarities: 10 min. exposure, quenching, T= 2300°C

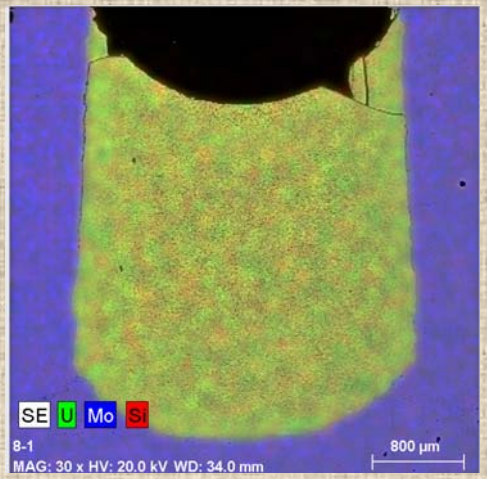
GPRS28

60 mol.% SiO_2 by synthesis

GPRS26

50 mol.% SiO_2 by synthesis

GPRS24

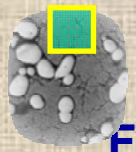


40 mol.% SiO_2 by synthesis

GPRS23

30 mol.% SiO_2 by synthesis

Liquid phase composition measurements



Fully melted

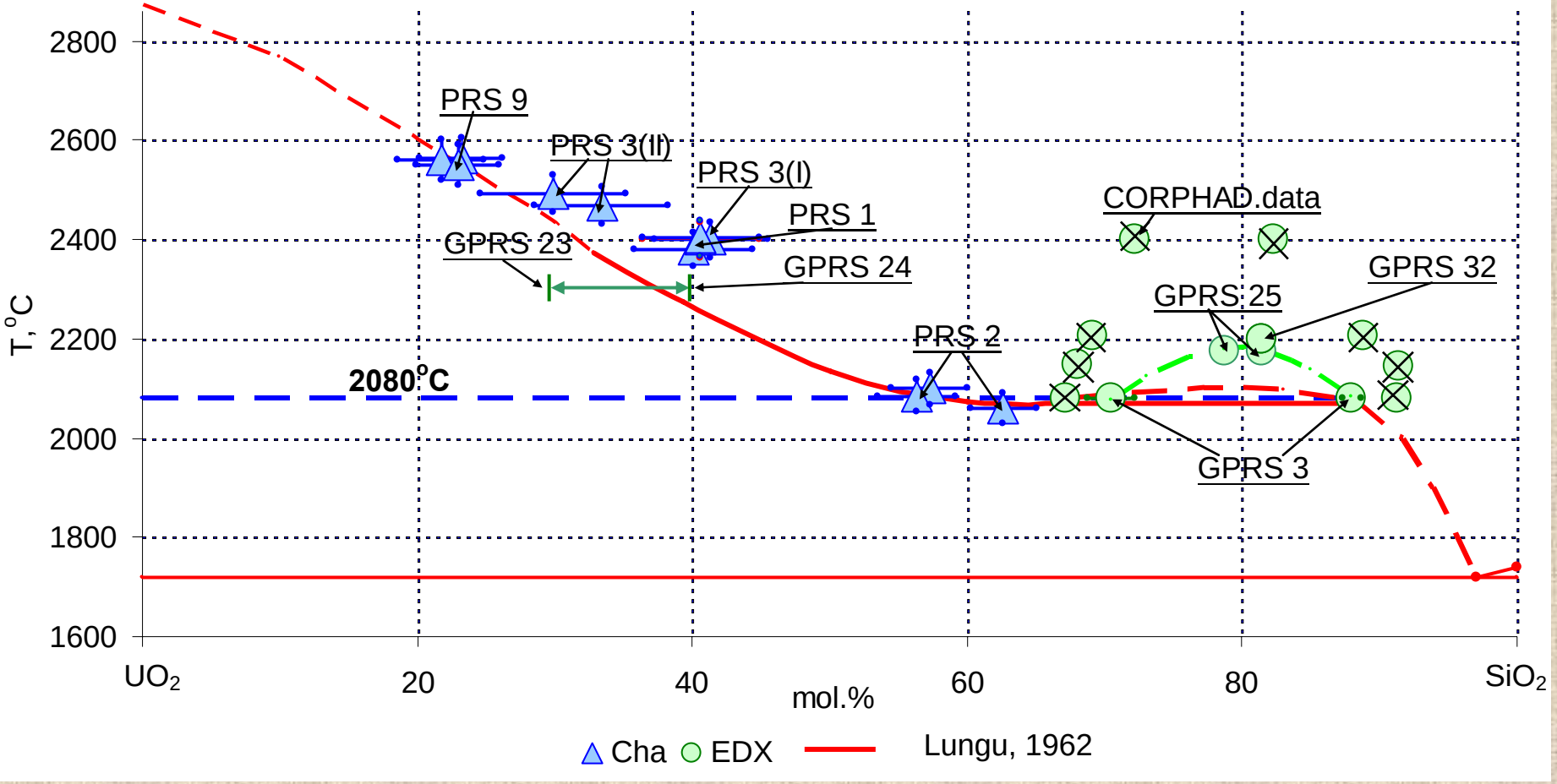
Fully melted

Fully melted

60.4 mol.% SiO_2

✓The liquidus line at the 2300°C isotherm passes between 30 and 40 mol.% SiO_2

Test results on $UO_2 – SiO_2$ system



- ✓The MG boundaries have been specified (CORPHAD data revision)
- ✓The MG critical point is located between 1975 and 2200°C
- ✓T_{liq} was determined in PRS9 test by VPA IMCC
- ✓ Liquidus point composition at 2300 C is between 30 and 40 mol % of silica

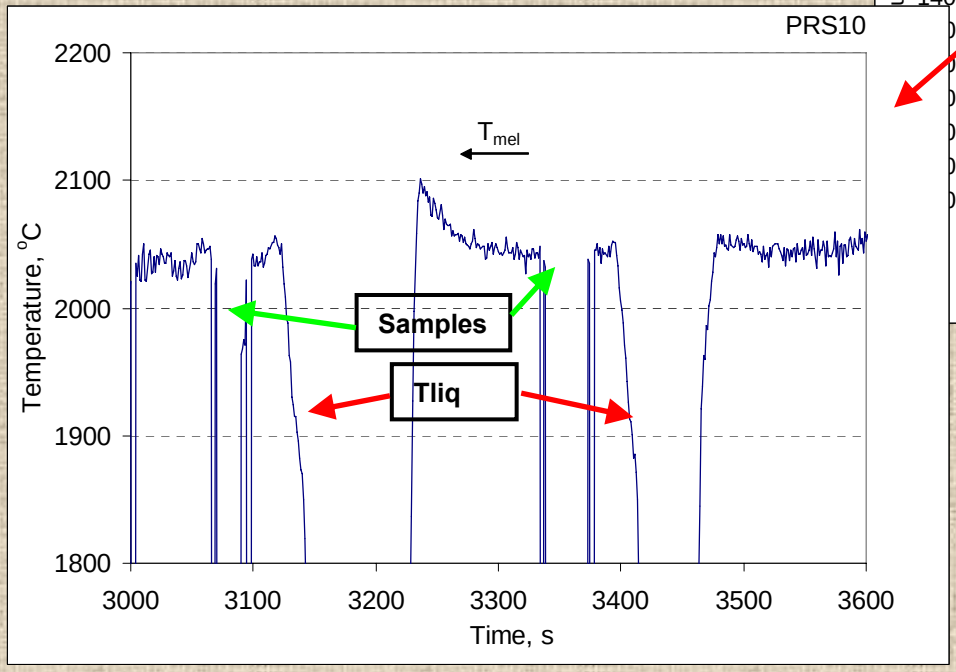
UO_2 - CaO system: PRS 10 test results

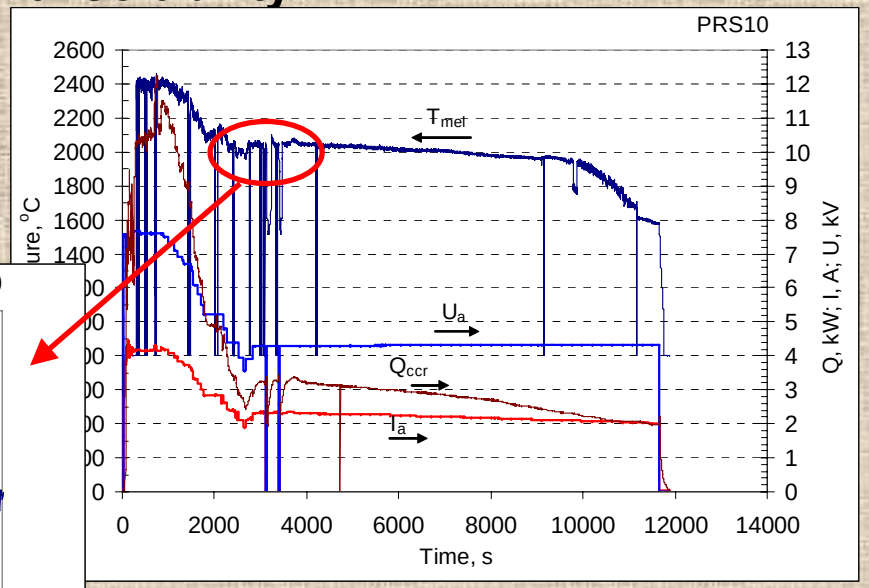
➢Experimental objectives

- Determination of the liquidus temperature
- Determination of the components final solubility in the formed solid solutions

➢Charge composition

- Mol% 36.2UO_2 + 63.8CaO



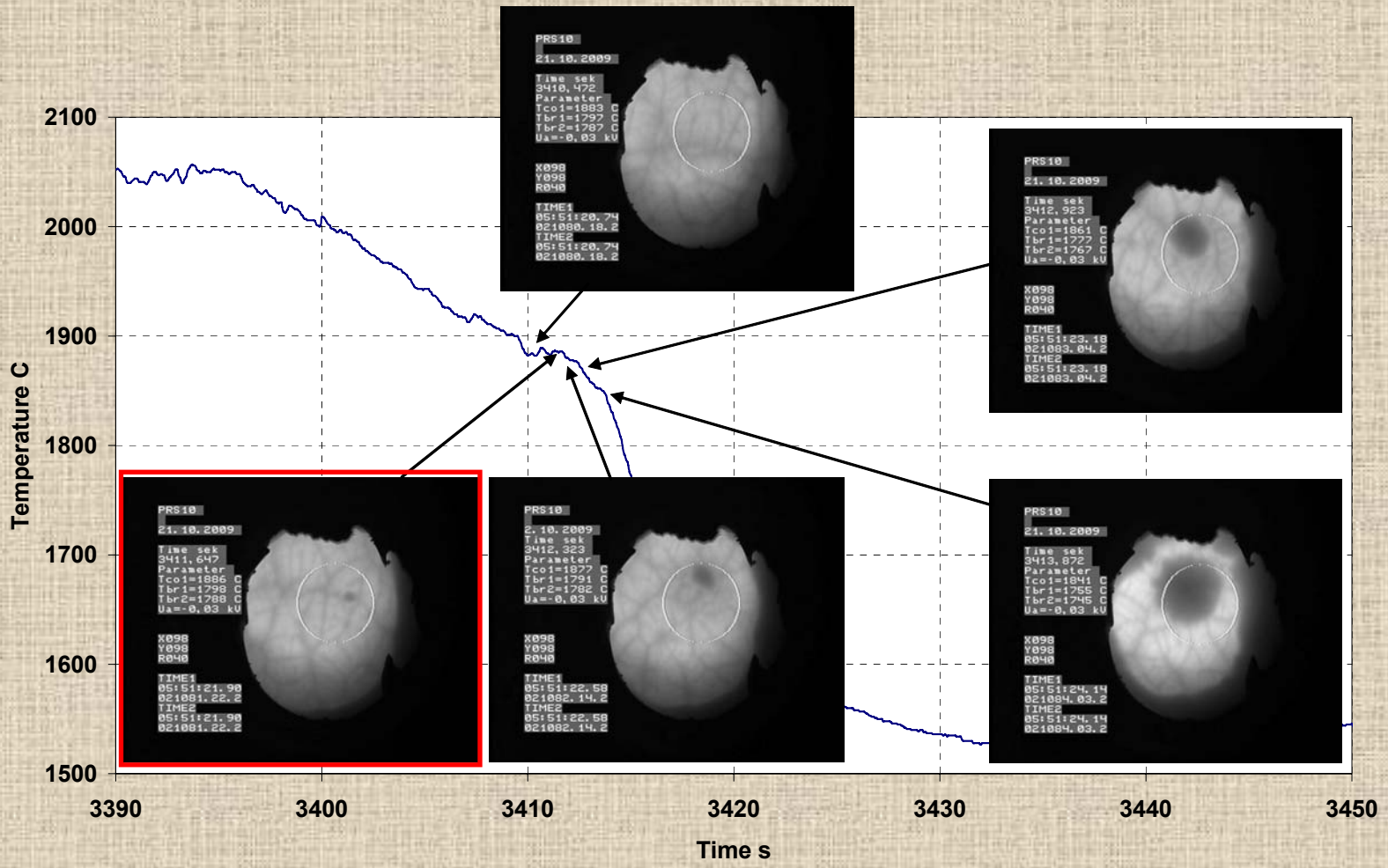


✓ From 4000 s, the pool was pulled out from inductor at 8.5 mm/h for 2 hours. This has ensured close to equilibrium crystallization and the eutectic liquid displacement into the ingot upper part

✓T_{liq} was measured 2 times by VPA IMCC with melt sampling

UO_2 - CaO system: PRS 10 test results (2)

- **VPA IMCC: Example of thermogram # 2 from the test showing melt surface**

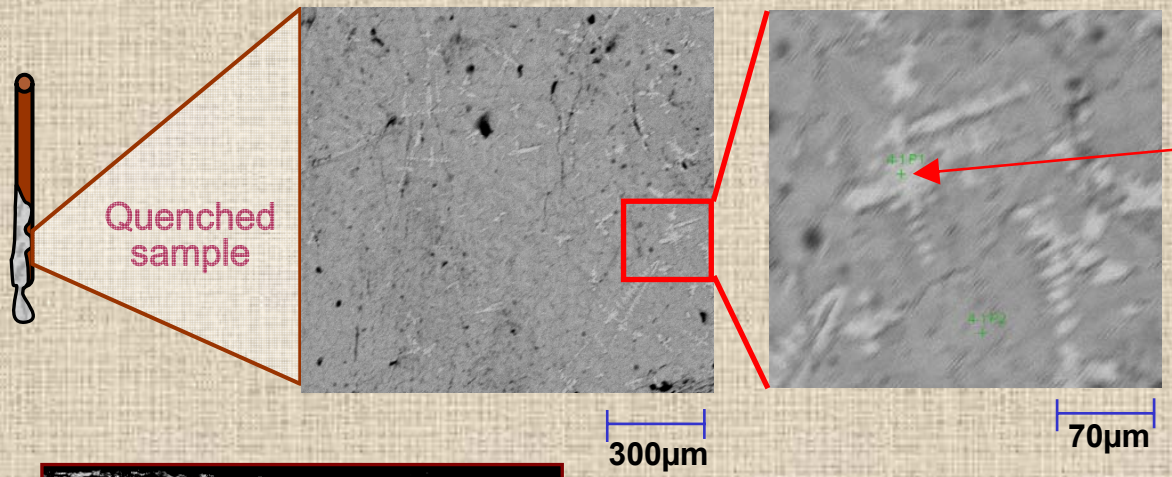


- ✓ **Results of T_{liq} measurements: 1876, 1880°C, ⇨ T_{liq}=1878±30°C**

UO_2 - CaO system: PRS 10 test results (3)

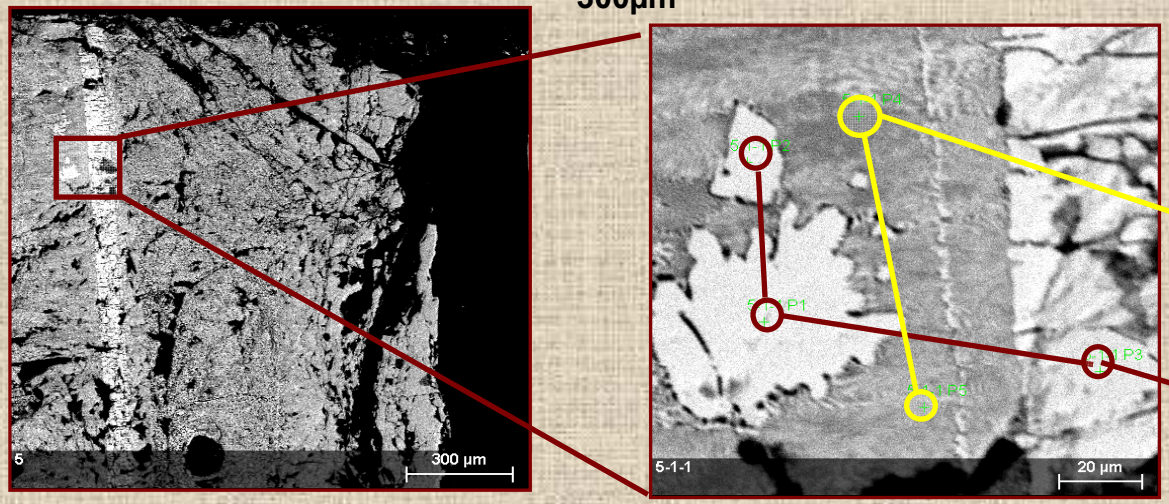
➢SEM/EDX analysis of the melt sample (top) and ingot periphery (bottom)

✓Dendritic microstructure of the melt sample



Primary crystallization phase

	UO_2	CaO
	mol.%	
P1	53.8	46.2



Sample	ChA	XRF	EDX
	UO_2 mol.%		
№1	38.1	41.4	34.9
№2	35.7	38.6	33.9

eutectic		UO_2	CaO
EDX	mass %	71.4±1.3	28.6±1.0
	mol%	34.1±0.4	65.9±0.8

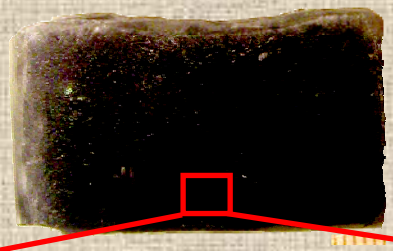
1st phase		UO_2	CaO
EDX	mass %	87.3±1.4	12.7±0.5
	mol%	58.9±0.8	41.1±0.4

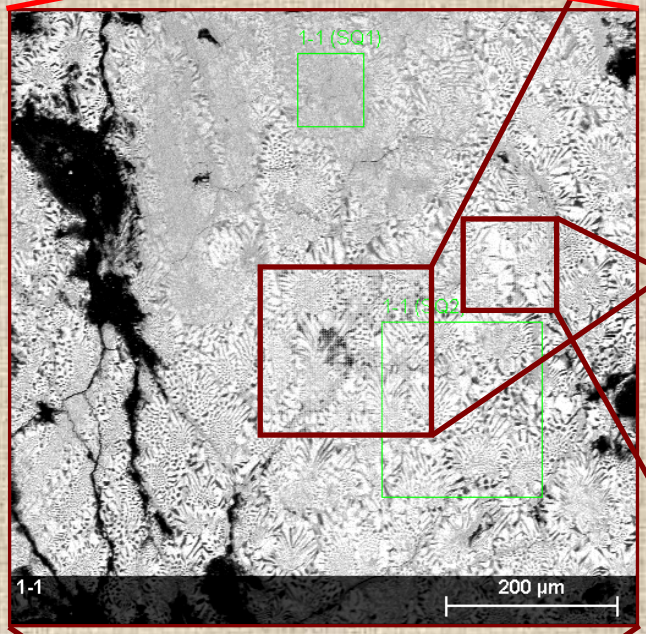
✓Compositions of melt samples of the unsaturated solid solution have been determined

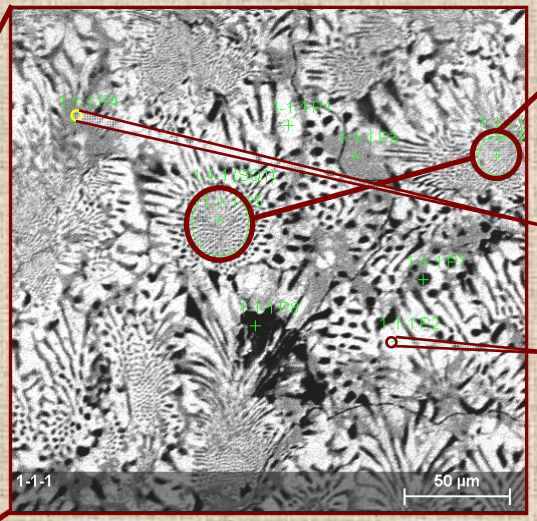
✓ There is a discrepancy between the results of SEM/EDX and (XRF+ChA)

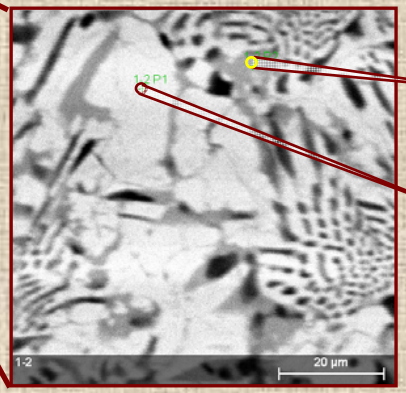
UO_2 - CaO system: PRS 10 test results (4)

➢SEM/EDX analysis of the ingot (central zone)









Eutectic		UO_2	CaO
EDX	mass %	69.1±0.7	30.9±0.2
	mol%	31.8±0.3	68.2±0.3

Eutectic		UO_2	CaO
EDX	mass %	70.4±1.0	29.6±1.3
	mol%	33.1±0.2	66.9±1.3

2nd phase		UO_2	CaO
EDX	mass %	68.7	31.3
	mol%	31.3	68.7

1st phase		UO_2	CaO
EDX	mass %	83.3	16.7
	mol%	50.8	49.2

Phase mix		UO_2	CaO
EDX	mass %	61.0	39.0
	mol%	24.5	75.5

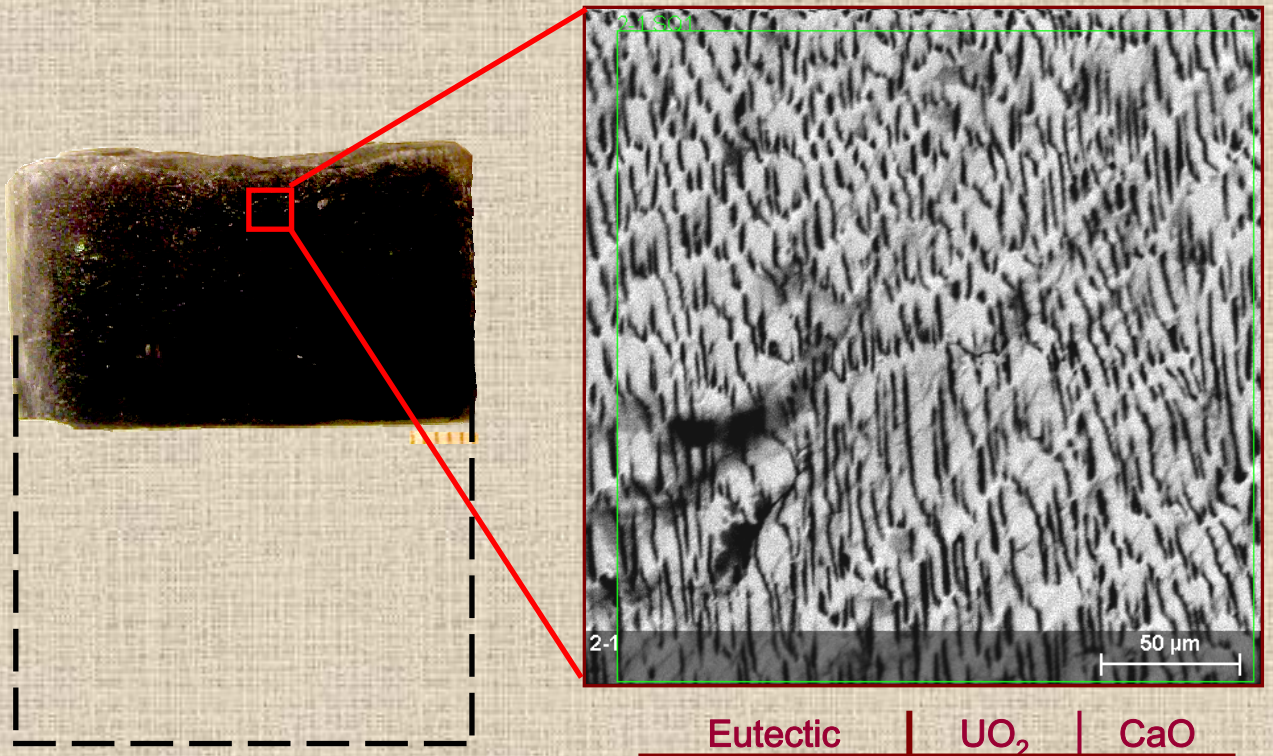
1st phase		UO_2	CaO
EDX	mass %	81.1	18.9
	mol%	47.2	52.8

Composition of the saturated solid solution

✓**A eutectic crystallization zone with a final solid solutions has been formed. Compositions of the eutectics and the solid solution have been determined**

UO_2 - CaO system: PRS 10 test results (5)

➢SEM/EDX analysis of the ingot (eutectic zone)

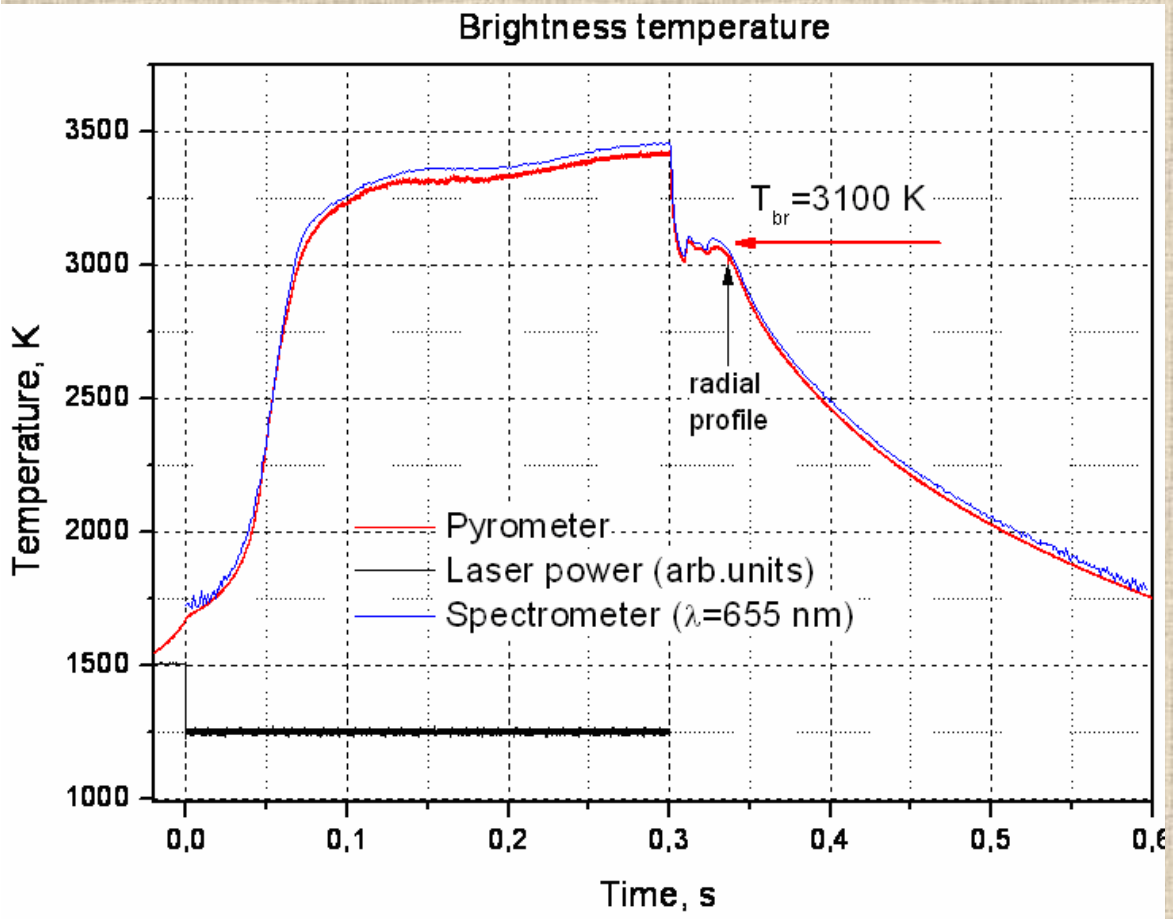


Eutectic		UO_2	CaO
EDX	mass %	72.0±1.8	28.0±1.4
	mol%	34.8±0.6	65.2±1.6

✓The eutectic composition has been determined by EDX in the eutectic crystallization zone without solid solutions

CaO Melting Point Measured by LPH in IVTAN

Experimental Thermogram LPH2



Peculiarities of CaO:

- Low absorption coefficient below 1500-2000K
- Boiling temperature of approximately 3300K, which is close to melting temperature

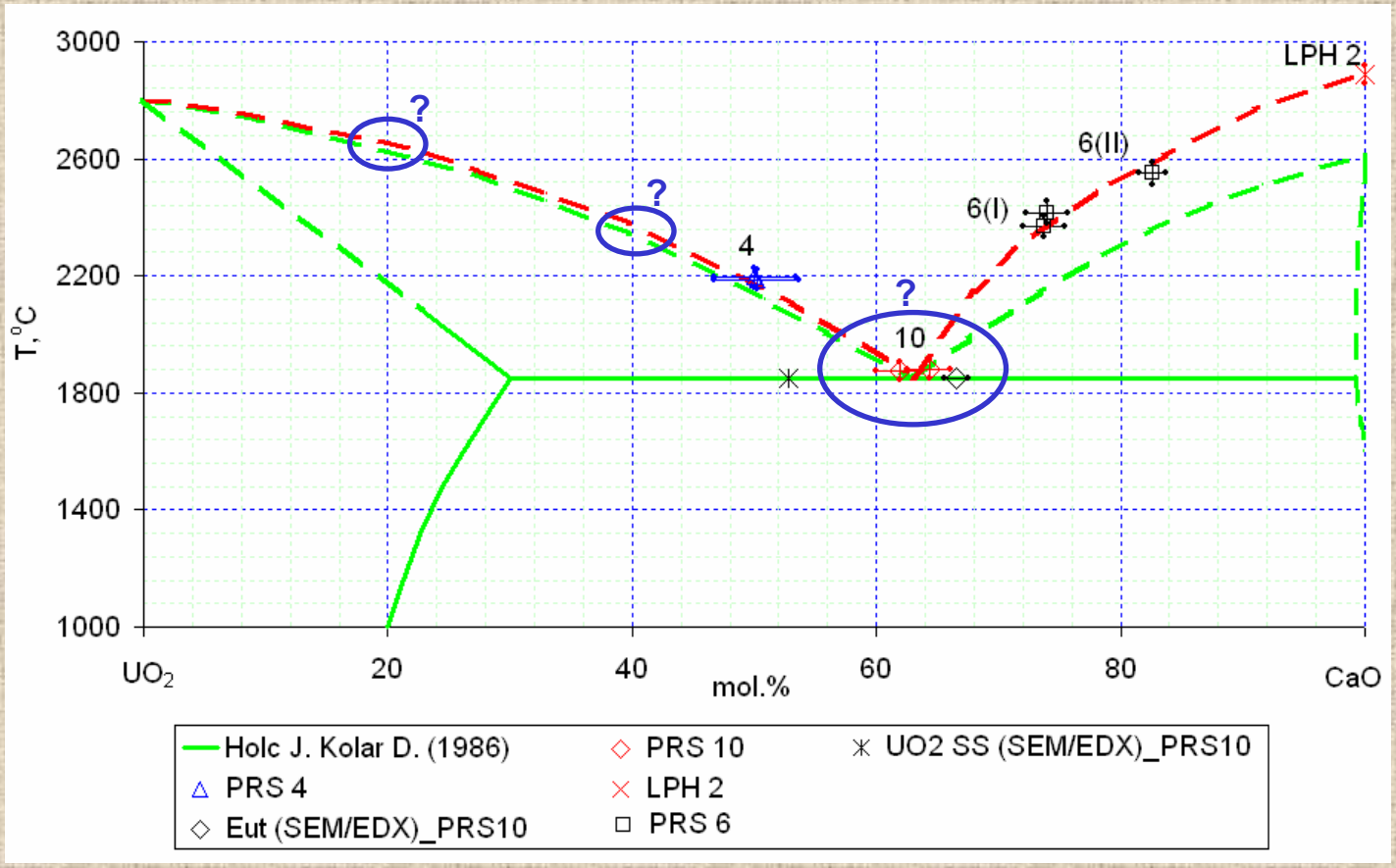
-Specimens melting procedure:

- Preliminary heating up to 1750K
- Controlled heating with a profiled laser pulse
- Coupling temperature measurement with a high-speed spectropyrometer
- Melt surface temperature fields registration with a high-speed camera
- Thermograms mathematical processing

✓**Supposing that ε=0.85-0.9→T_{melt}= 3160 ± 30K**

✓**ε for CaO is to be refined later**

Test results on UO_2 - CaO system



- ✓ T_{liq} was determined in PRS10 test. The temperature of CaO melting was refined in LPH2 test SEM/EDX was used for determining compositions of the eutectics and the saturated solid solution
- ✓ In future, it is planned to measure T_{liq} for the UO_2-rich compositions and perform a test with the eutectic composition for measuring the eutectic temperature and check of $CaUO_3$ and Ca_2UO_4 compounds

UO_2-SiO_2-FeO system:GPRS #33-36 test results

- **Experimental objectives**
  - Determination of the liquidus temperature
  - Determination of the ternary eutectic point
- **Annealing, melting and quenching in the Galakhov microfurnace (estimation of ternary eutectic position)**

Test	Content, mol.%			Temperature, °C	Exposure time, min	Note
	UO_2	SiO_2	FeO			
GPRS33	5.0	70.0	25.0	1100	60	Annealing
				2100	5	Melting and quenching
GPRS34	10.0	80.0	10.0	1100	60	Annealing
				1850	5	Melting and quenching
GPRS35	20.0	73.0	7.0	1100	60	Annealing
				1950	5	Melting and quenching
GPRS36	1.7	65.5	32.8	1100	60	Annealing
				1300	20	Melting
				1300-900	240	Cooling at 100°C/h

✓ UO_2 of >99.0 % purity, SiO_2 of 99.99% purity, charge mass – 150 mg

✓ Posttest analysis of the tests are underway

Joint publications with collaborators

- V.I. Almjashev, M. Barrachin, S.V. Bechta, D. Bottomley, F. Defoort, M. Fischer, V.V. Gusarov, S. Hellmann, V.B. Khabensky, E.V. Krushinov, D.B. Lopukh, L.P. Mezentseva, A. Miassoedov, Yu.B. Petrov, S.A. Vitol. Eutectic crystallization in the $FeO_{1,5}$–UO_{2+x}–ZrO_2 system // Journal of Nuclear Materials, 389, p. 52-56 (2009).

- S. Bakardjieva, M. Barrachin, S. Bechta, D. Bottomley, L. Brissoneau, B. Cheynet, E. Fischer, C. Journeau, M. Kiselova, L. Mezentseva, P. Piluso, T. Wiss. Improvement of the European thermodynamic database NUCLEA // Journal of Progress in Nuclear Energy, 52, p. 84-96 (2010).

- V.I. Almjashev, M. Barrachin, S.V. Bechta, D. Bottomley, F. Defoort, M.Fischer, V.V. Gusarov, S. Hellmann, V.B. Khabensky, E.V. Krushinov, D.B.Lopukh, L.P. Mezentseva, A. Miassoedov, Yu.B. Petrov, S.A. Vitol. Phase equilibria in the FeO1+x –UO2 –ZrO2 system in the FeO1+x-enriched domain // Journal of Nuclear Materials (2010). Accepted Manuscript, doi: 10.1016/j.jnucmat.2010.02.020

Concluding remarks

- ✓ The temperature of CaO melting has been significantly refined for the CaO-UO_2 system
- ✓ With exception for ZrO_2-FeO_y, other binary systems are studied in accordance with the Work Plan. The works are close to completion
- ✓ Study of the UO_2-SiO_2-FeO ternary system have been started
- ✓ Plans for quarters # 8 - 9:

- Complete the UO_2-SiO_2 and UO_2-CaO systems and start a paper preparation
- Continue study of the ZrO_2-FeO_y system
- Continue investigations of the UO_2-SiO_2-FeO system
- Start study of the CaO-UO_2- FeO system
- Continue study of the U-Zr-O system by LPH