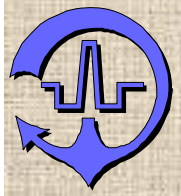

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Progress report on the ISTC project #3813: Phase relation in corium systems (PRECOS)

Presented by S. Bechta

18th CEG-SAM meeting
St. Petersburg, Russia
September 28-30, 2010

Contents

- General information
- Project objectives
- PRECOS test matrix
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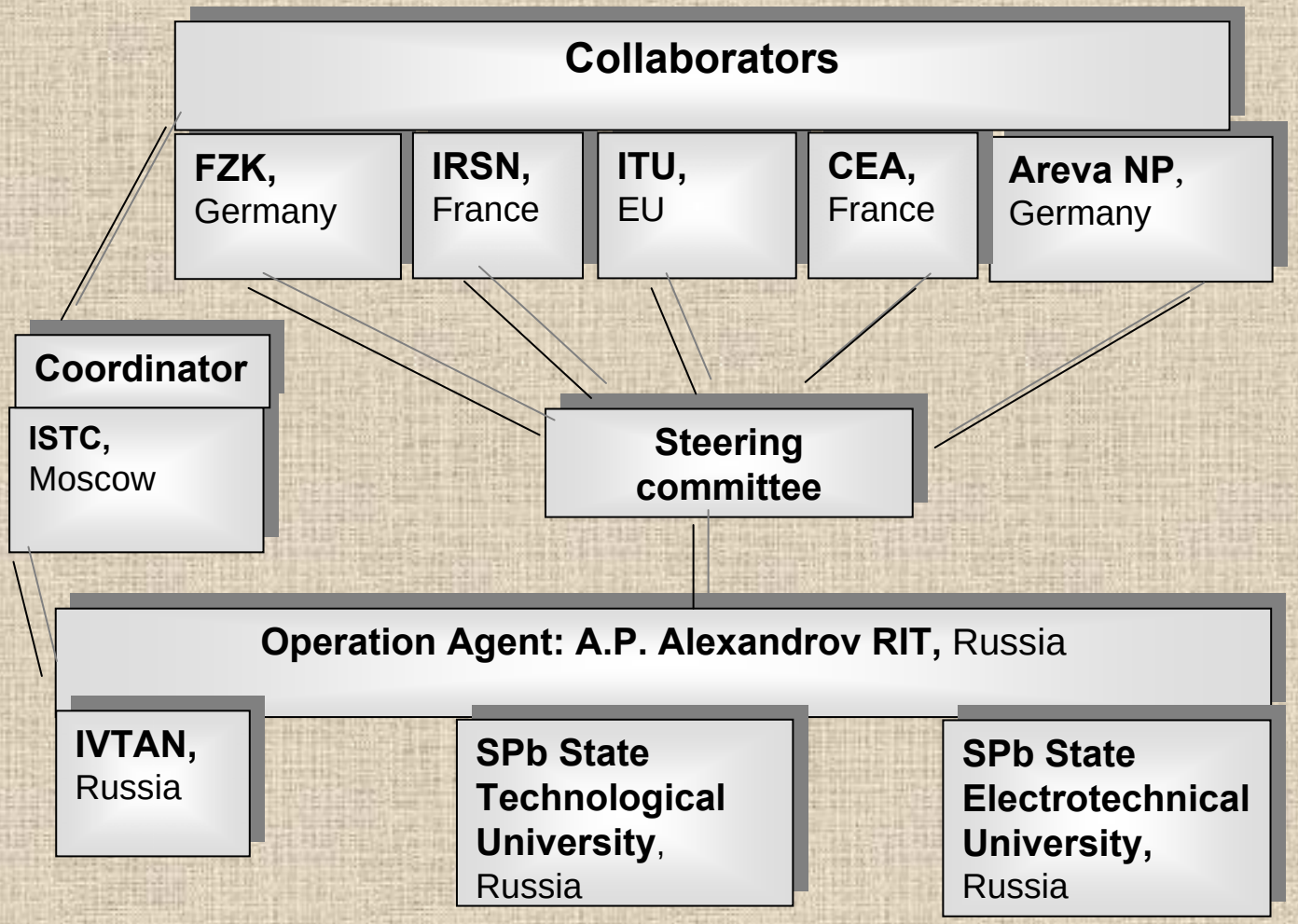
- Test results:
  - UO_2-CaO system
  - UO_2-SiO_2- FeO system
  - UO_2-CaO- FeO system
- Concluding remarks

PRECOS project general information



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	Atm	Experimental data	Priority level	Number of tests scheduled /carried out
1	U-Zr-Fe-O	Argon	Selected points (liquidus, solidus, tie-lines in the miscibility gap)	1	6/8[1]
2	ZrO_2 - FeO_y	Air and p_{O_2} control	liquidus, solidus, solubility limits	2	3/3[2]
	UO_2 - SiO_2	Neutral	liquidus, solidus, solubility limits, eutectic point	1	7/(5[3]+40[4])
	CaO - UO_2			1	7/7[3]
3	UO_2 – FeO – SiO_2		liquidus, solidus, solubility limits, tie-lines in the miscibility gap, ternary eutectic point	1	10/(1[3]+4[4])
	UO_2 – FeO – CaO		liquidus, solidus, solubility limits, ternary eutectic point	1	10/1[3]
	ZrO_2 - FeO - SiO_2		ternary eutectic point	2	2/0
	ZrO_2 - FeO - CaO		ternary eutectic point	2	2/0
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	3/0

Notes: 1-LPH (Zr-O), 2- HTM, 3- VPA IMCC, 4- VPA in Galahov microfurnace

Scope of work in quarters 8-9

- ✓ Experiments in the UO_2-CaO, UO_2-FeO-CaO, UO_2-FeO-SiO_2 systems have been conducted. Post-test analysis of samples is in progress
- ✓IVT RAN setup with laser heating has been additionally equipped with 300 mW diode laser for specimen lighting
- ✓IVT RAN setup with laser heating has been used for the verification experiments on previously studied Zr-O and ZrO_2-FeO systems
- ✓Construction work necessary for getting a license on uranium handling has been completed. The license is expected to be issued in December 2010; after that the U-Zr-Fe-O studies will be started

Scope of work in quarters 8-9 (2)

System	Test	Objective	Status
UO_2-CaO	PRS 11,12	Determination of the liquidus temperature. Determination of the components final solubility in the formed solid solutions	Tests done Post test analysis in progress
UO_2-FeO-SiO_2	GPRS 33-36 PRS13	T_{liq}, T_{sol}, solubility limits, tie-lines in the miscibility gap, ternary eutectic point	
UO_2-FeO-CaO	PRS14	T_{liq} determination by VPA IMCC. Determination of eutectic composition	

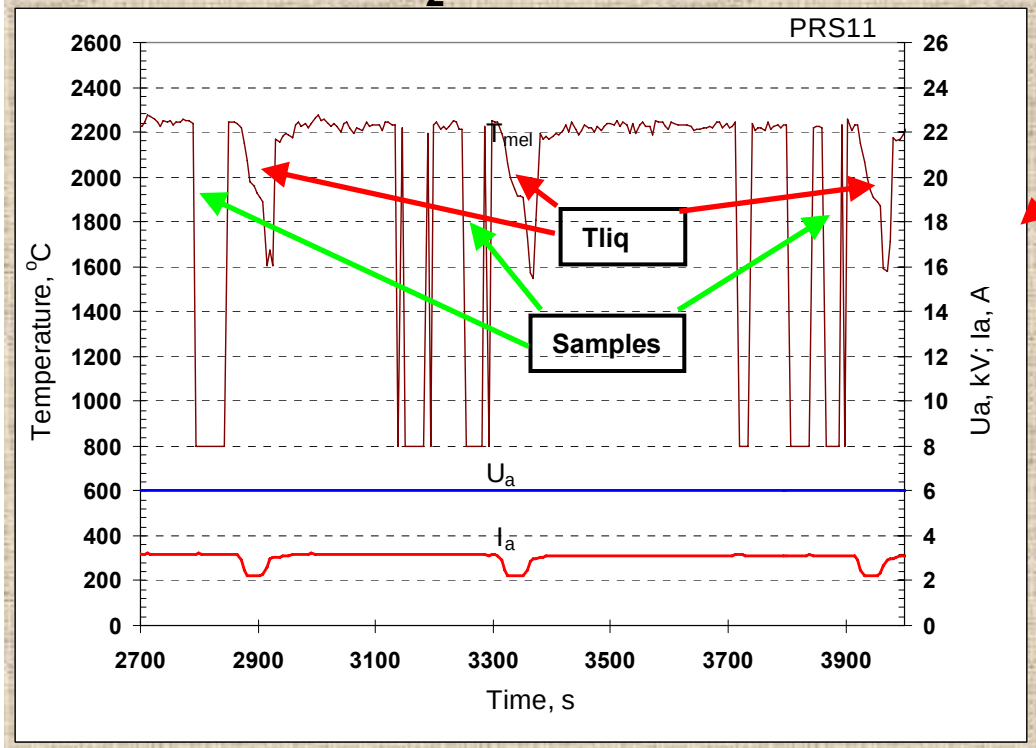
UO_2 - CaO system: PRS 11 test results

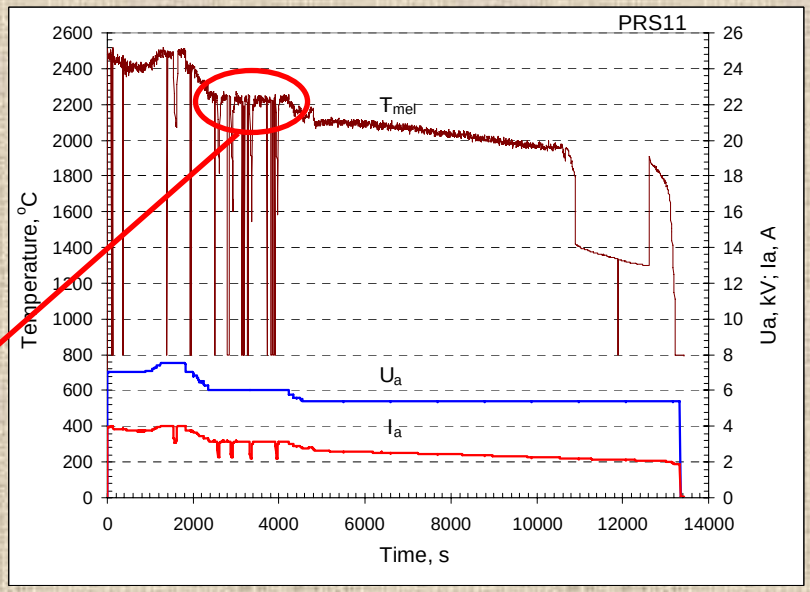
➢Experimental objectives

- T_{liq} determination
- Determination of the components final solubility in the formed solid solutions

➢Charge composition

mol.% 30UO_2 + 70CaO



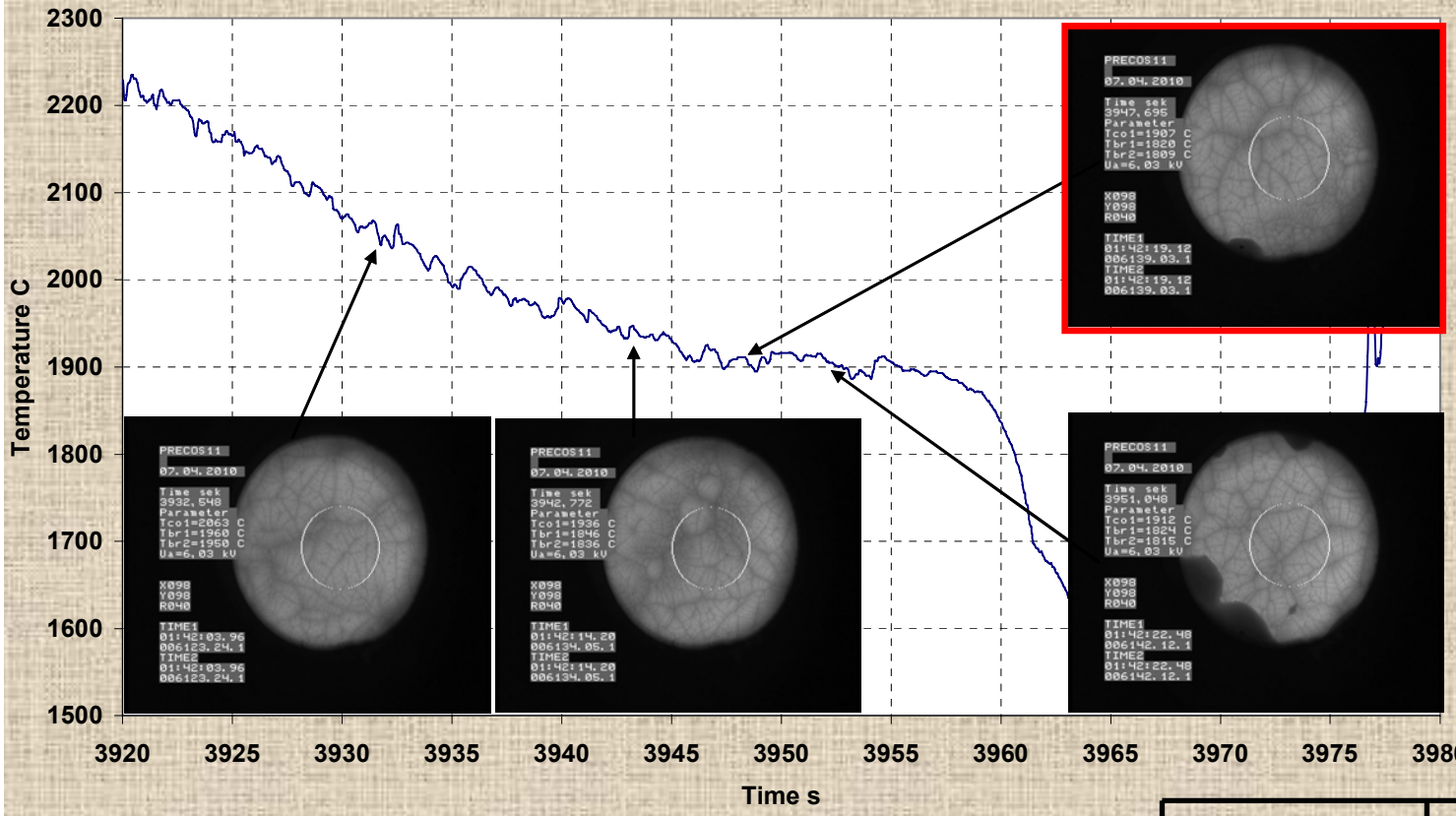


✓ From 4829 s, the pool was pulled out from inductor at 8.5 mm/h for 2.4 hours. This has ensured close to equilibrium crystallization and the eutectic liquid displacement into the ingot upper part

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

UO_2 - CaO system: PRS 11 test results (2)

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



Melt samples composition

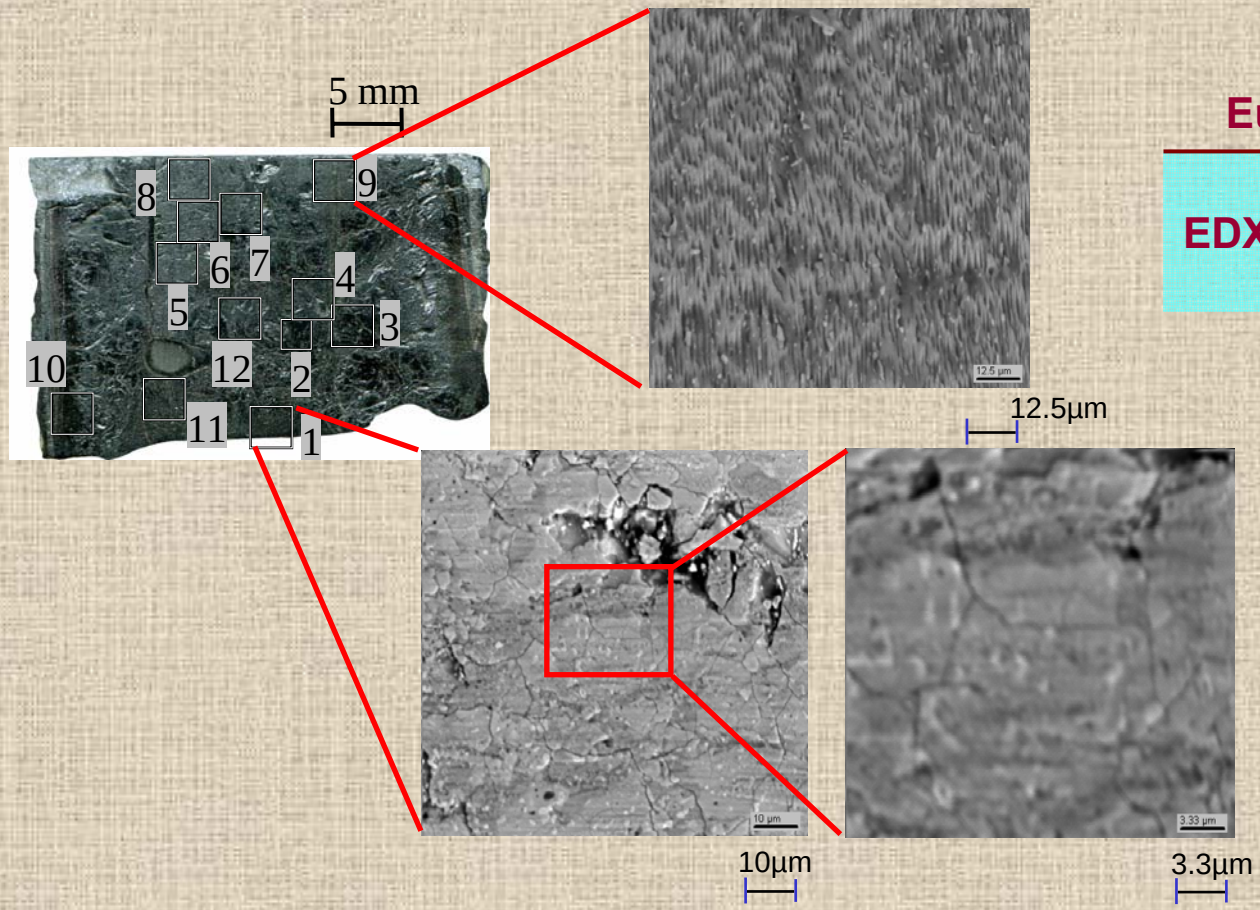
Sample	Cha	XRF
	UO_2 mol.%	
#1	30.5	32.0
#2	30.1	32.9
#3	30.8	34.5

- ✓ **Results of T_{liq} measurements: 1912, 1910, 1907°C**

SEM/EDX in progress

UO_2 - CaO system: PRS 11 test results (3)

➢SEM/EDX analysis of the ingot



Eutectic		UO_2	CaO
EDX	mass %	69.7	30.3
	mol%	32.4	67.6

Ca_2UO_4

- ✓ Ingot practically consists of Ca_2UO_4 and small eutectic regions
- ✓ Eutectic composition is close to the chemical compound, and during the long-term exposure the crystallized eutectic regions undergo recrystallization

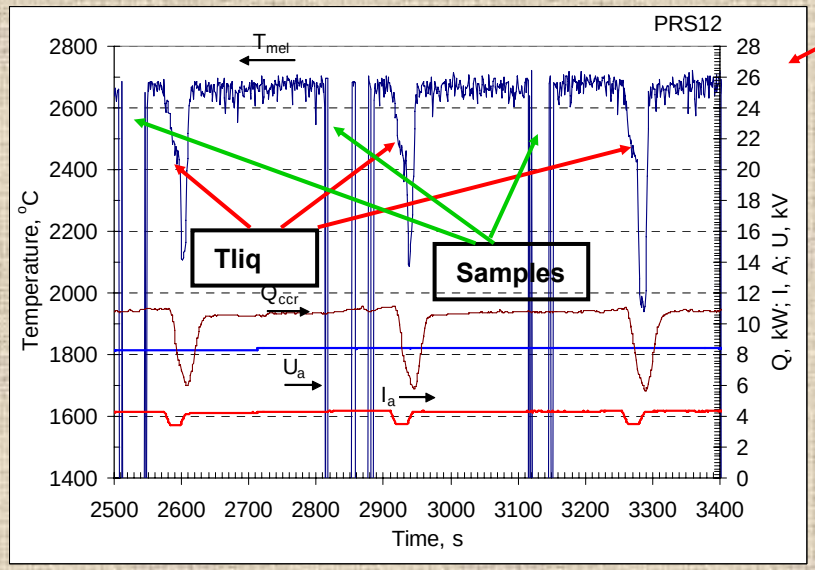
UO_2 - CaO system: PRS 12 test results

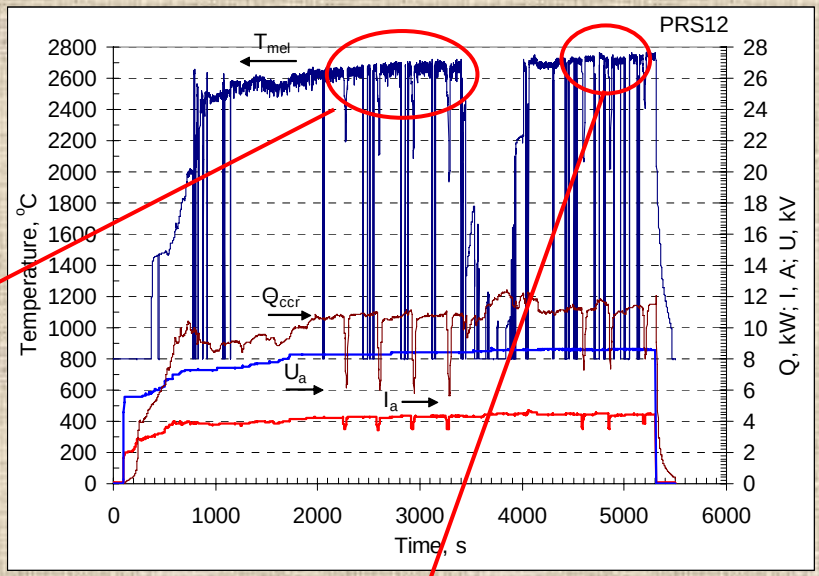
➢Experimental objectives

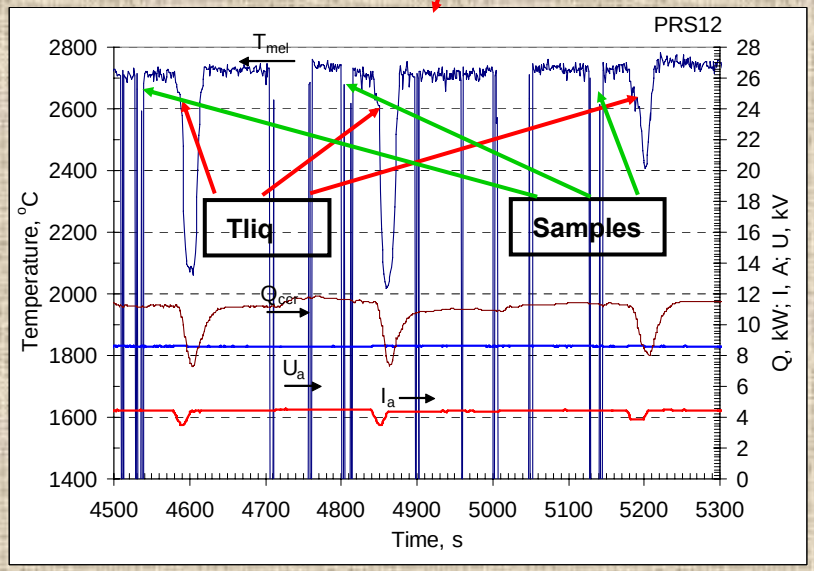
T_{liq} determination at high UO_2 content

➢Charge composition

mol.% 60UO_2 + 40CaO



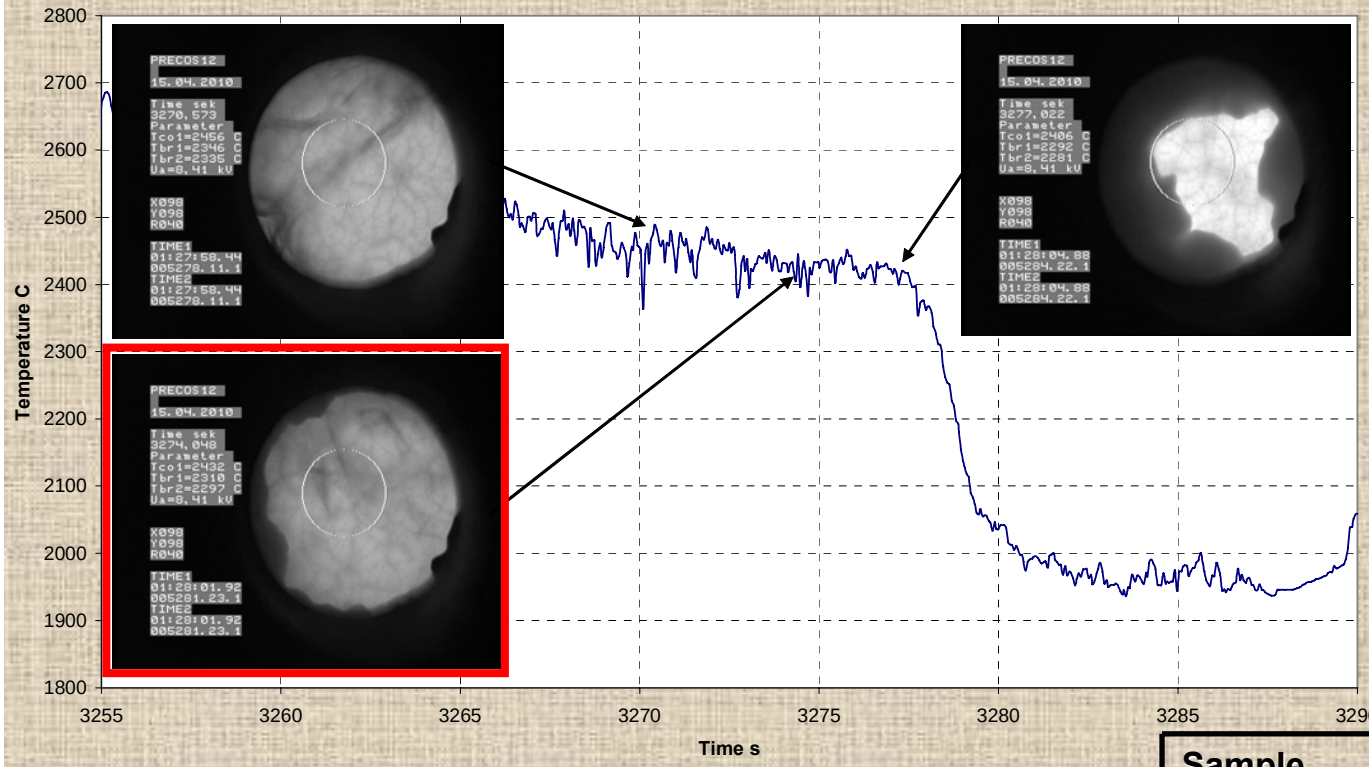




- ✓ Two melt compositions have been realized within one melting cycle
- ✓ 6 melt samples were taken and T_{liq} was measured 6 times by VPA IMCC

UO_2 - CaO system: PRS 12 test results (2)

- Charge composition, mol.% $60UO_2 + 40CaO$
- VPA IMCC: Fragment of the experiment thermogram 3 showing melt surface



✓ T_{liq} was measured 3 times: 2440, 2420 and 2432°C

SEM/EDX in progress

Melt samples composition

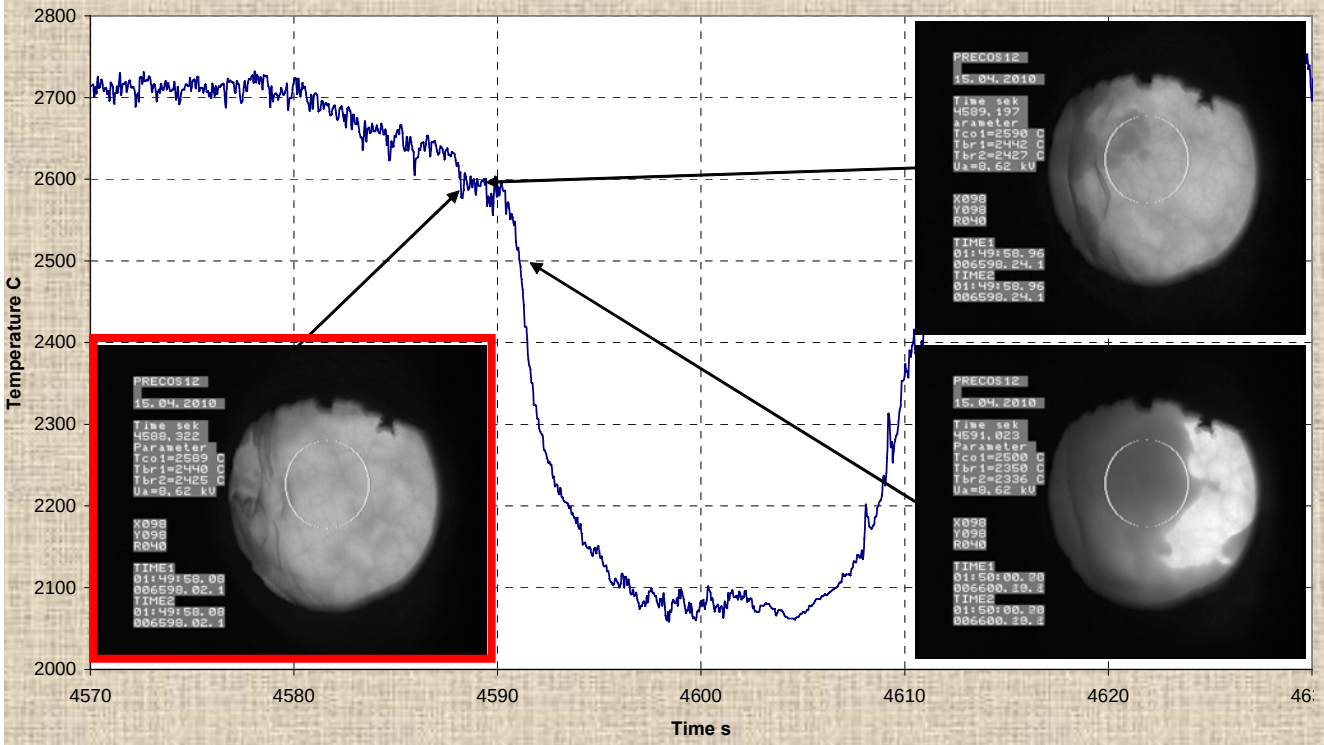
Sample	Cha	XRF
	UO_2 mol.%	
№1	57.3	55.03
№2	52.3	56.3
№3	59.3	55.1

UO_2 - CaO system: PRS 12 test results (3)

- **Charge composition (after CaO addition in to the melt)**

  mol.% $70UO_2 + 30CaO$

- **VPA IMCC: Fragment of the experimental thermogram 4 showing melt surface**



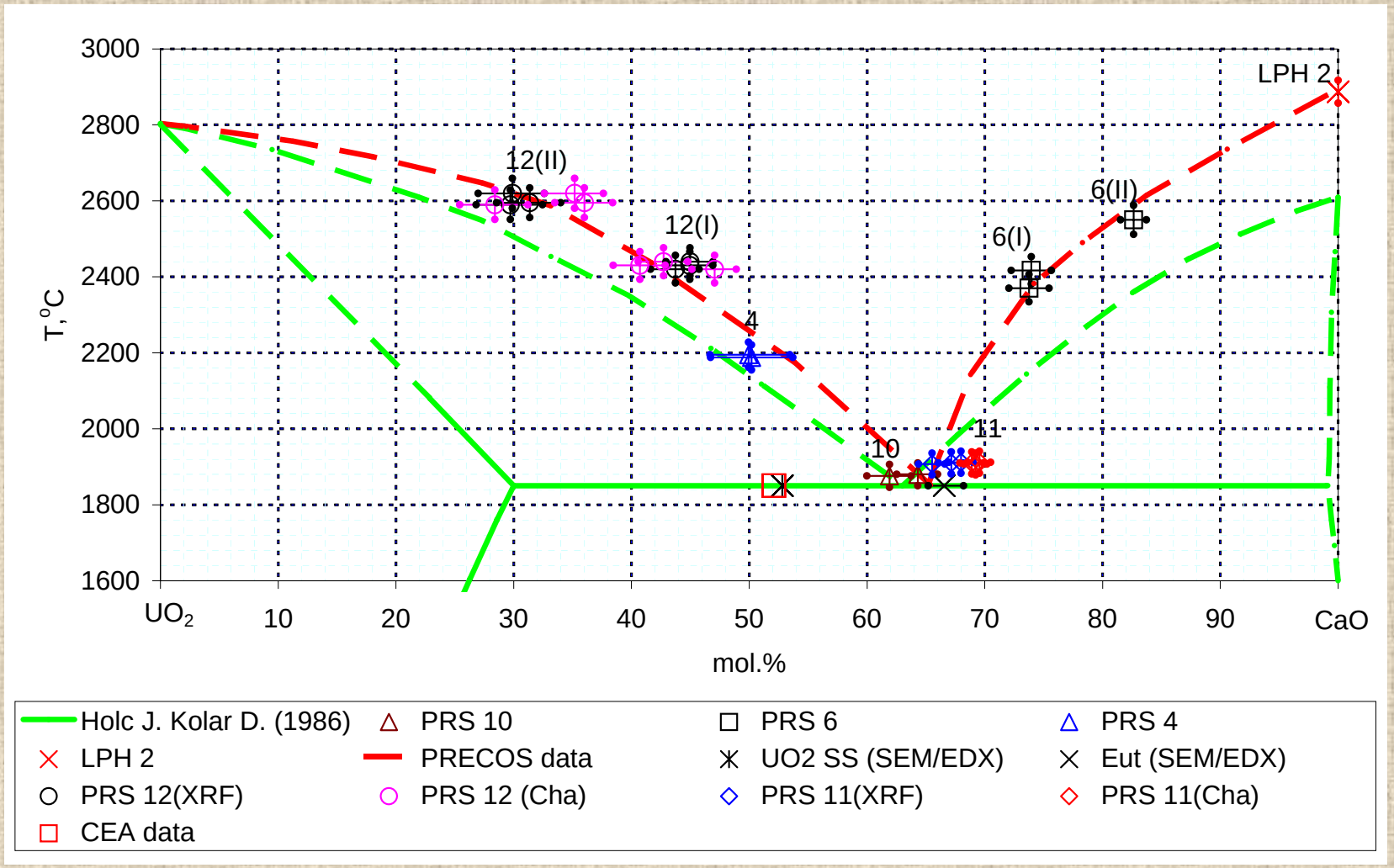
Melt samples composition

Sample	Cha	XRF
	UO_2 mol.%	
№4	71.6	70.3
№5	64.8	70.1
№6	64.0	68.6

- ✓ **T_{liq} was measured 3 times: 2589, 2620 and 2595°C**

SEM/EDX in progress

Test results on the UO_2 - CaO system



- ✓ **Compositions of the final solid solutions and the eutectics will be refined after SEM/EDX has been performed for PRS12**
- ✓ **The posttest analysis of samples from the corium ingot from VULCANO VP-U1, an ECOSTAR test, has detected CaO solubility in UO_2 (aproximately 47.9 мол.%) in one of the samples**

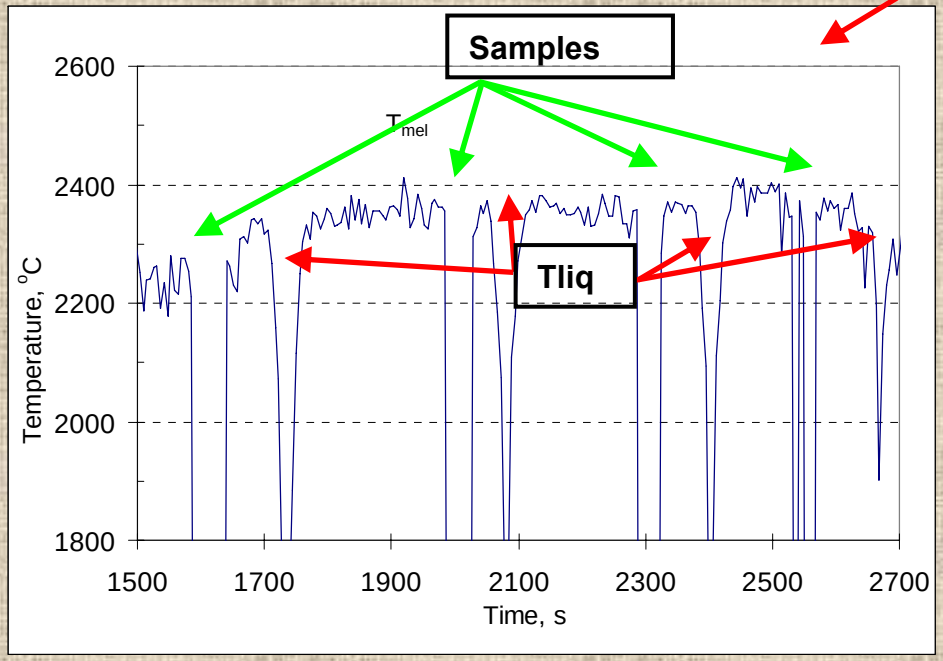
UO_2 – FeO – SiO_2 system: PRS 13 test results

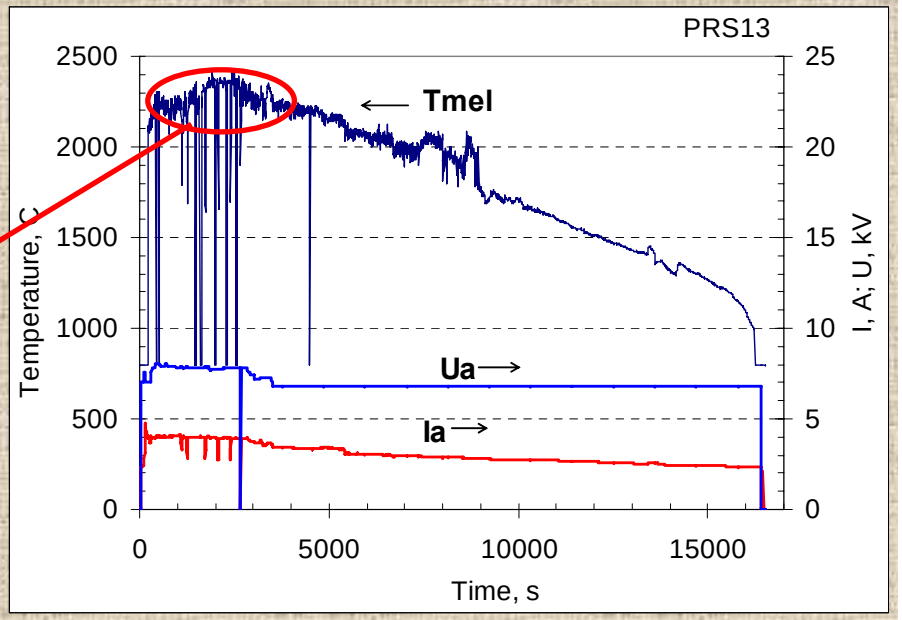
➢Experimental objectives

- T_{liq} determination by VPA IMCC.
- Determination of the ternary eutectic composition

➢Charge composition

mol.% 30.00 UO_2 + 46.67 FeO +23.33 SiO_2



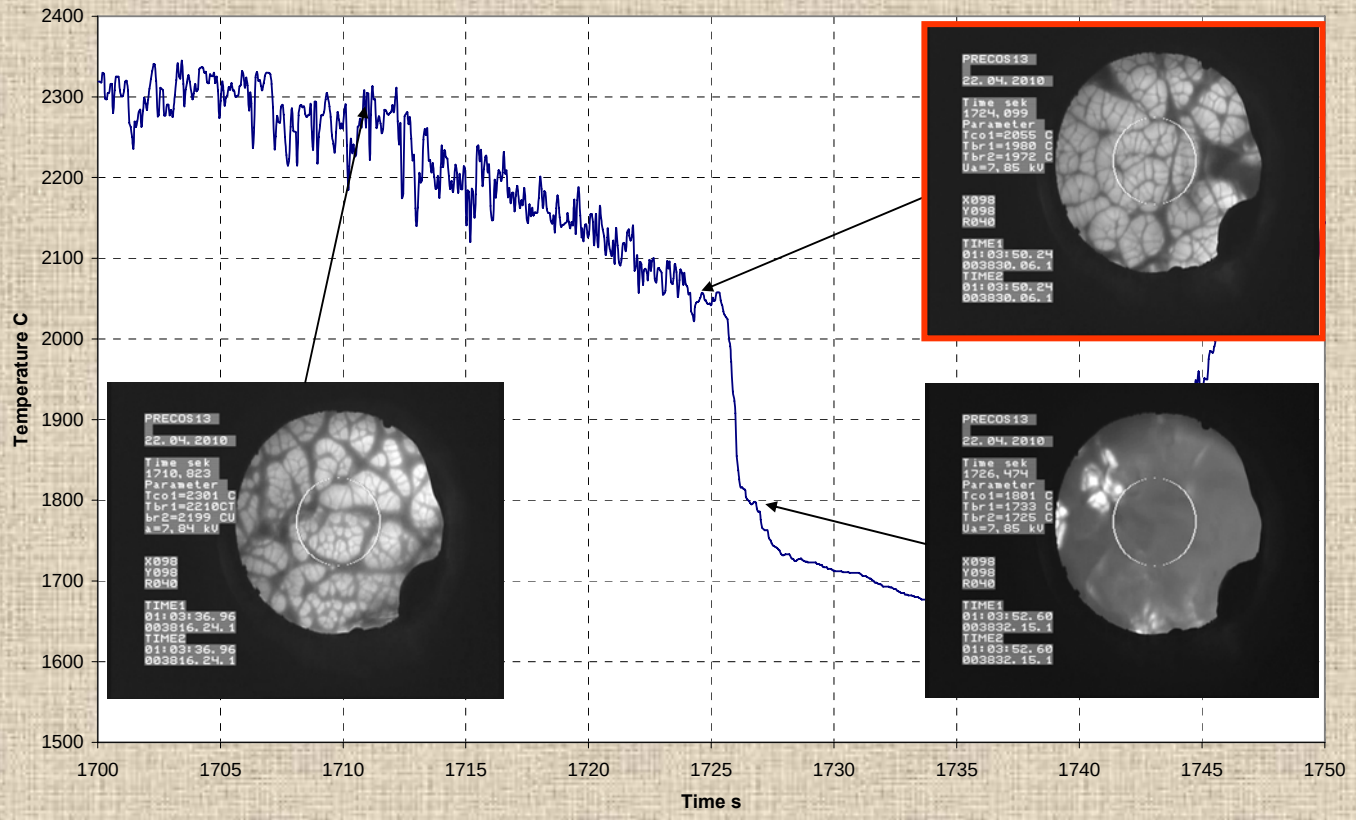


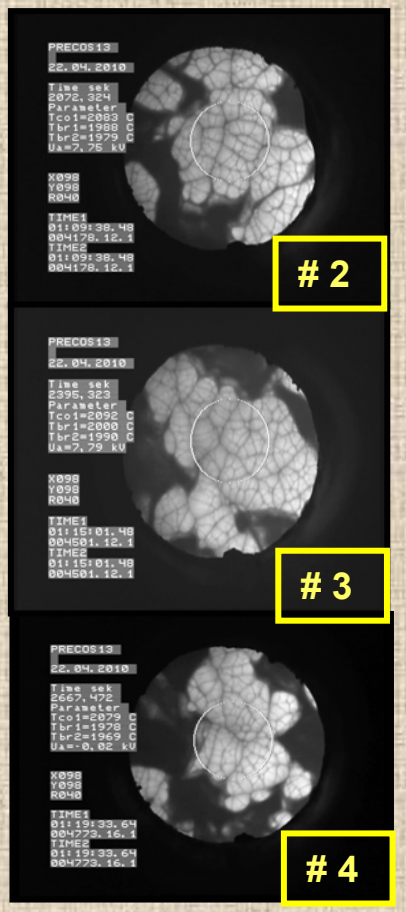
From 3276 s, the pool was pulled out from inductor at 9 mm/h for 3.6 hours. This has ensured close to equilibrium crystallization and the eutectic liquid displacement into the ingot upper part

✓T_{liq} was measured 4 times by VPA IMCC and accompanied by melt sampling

UO_2–FeO–SiO_2 system: PRS 13 test results (2)

- **VPA IMCC: Example of thermogram 1 from the test showing melt surface**





✓ Results of T_{liq} measurements: 2055, 2083, 2092, 2079°C

UO_2–FeO–SiO_2 system: PRS 13 test results (3)

➢Chemical analysis of melt samples

Samples	Melt samples composition						T_{liq}, °C
	mass %			mol.%			
	UO_2	FeO	SiO_2	UO_2	FeO	SiO_2	
1	55.63	30.71	13.66	23.93	49.65	26.42	2055±30
2	55.97	30.76	13.27	24.20	50.00	25.80	2083±30
3	55.22	31.07	13.70	23.64	50.00	26.36	2092±30
4	55.38	31.08	13.54	23.76	50.13	26.11	2080±30
Charge composition	63.01	26.08	10.91	30.00	46.67	23.33	

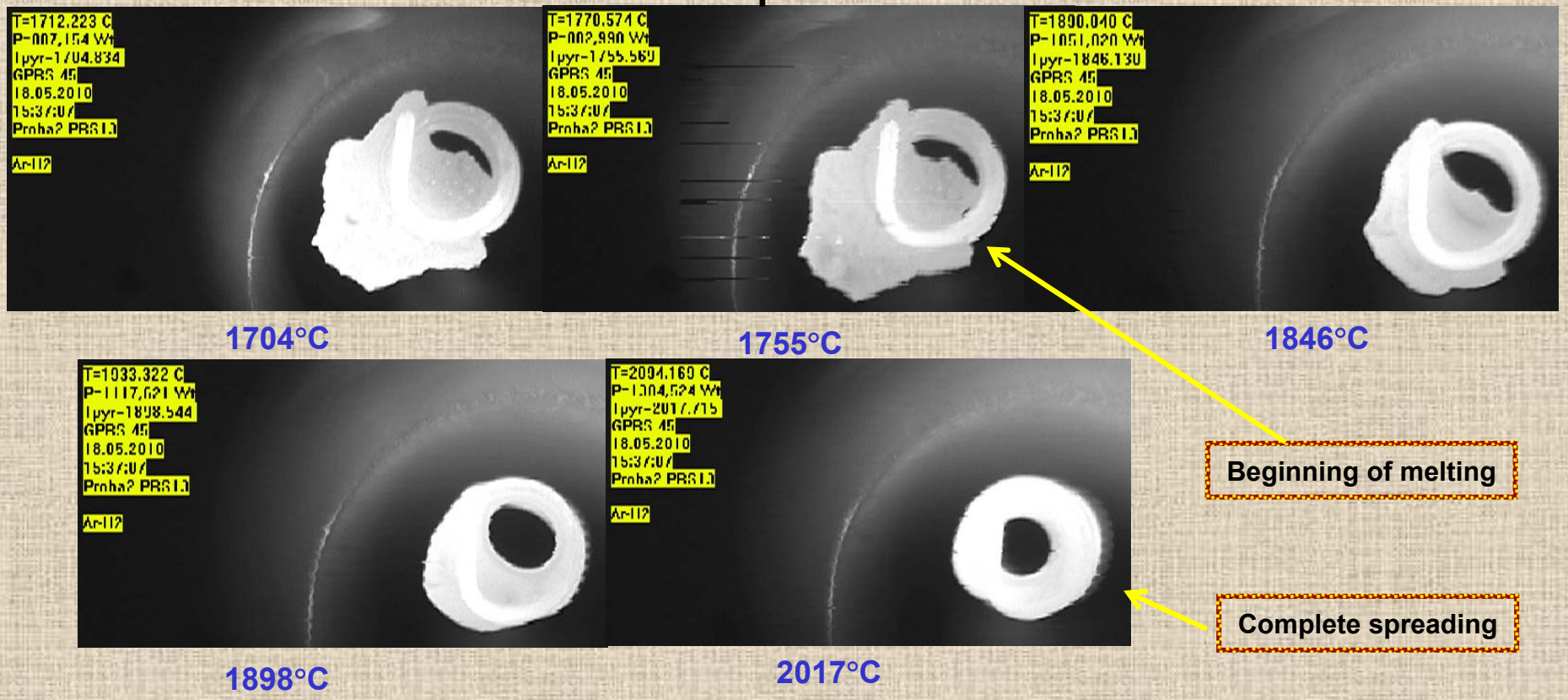
In progress:

- **SEM/EDX analysis of melt samples;**
- **chemical analysis of other fused products (ingot, crusts, dry spillages and aerosols) for composing the elemental material balance**

UO_2–FeO-SiO_2 system: PRS 13 test results (4)

➢ T_{liq} and T_{sol} determination in the Galakhov microfurnace

Sample 2

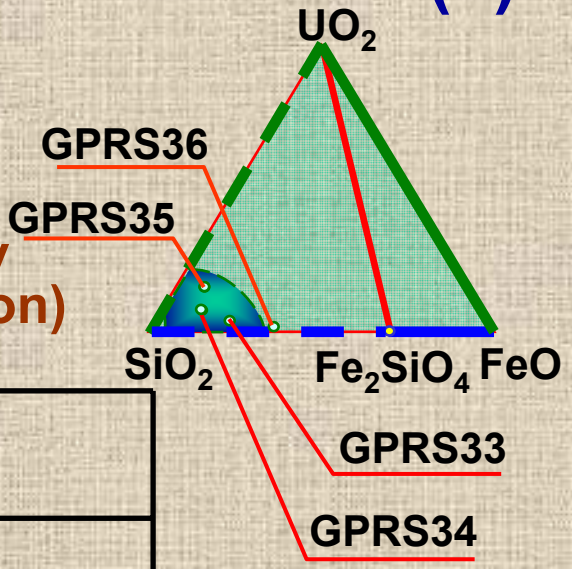


✓Visual polythermal analysis in the Galakhov microfurnace T_{sol}= 1755°C; T_{liq}=2017°C

✓T_{liq}, determined by the VPA IMCC (2083±30°C) and by the Galakhov method (2017°C) for the composition in question differ by 66°C, presumably, due to the interaction of the sample with the holder in the Galakhov microfurnace

UO_2-FeO-SiO_2 system: GPRS #33-36 test results (5)

- **Experimental objectives**
  - Study the miscibility gap boundaries
  - Determine ternary eutectic point
- **Annealing, melting and quenching in the Galakhov microfurnace (estimation of ternary eutectic position)**

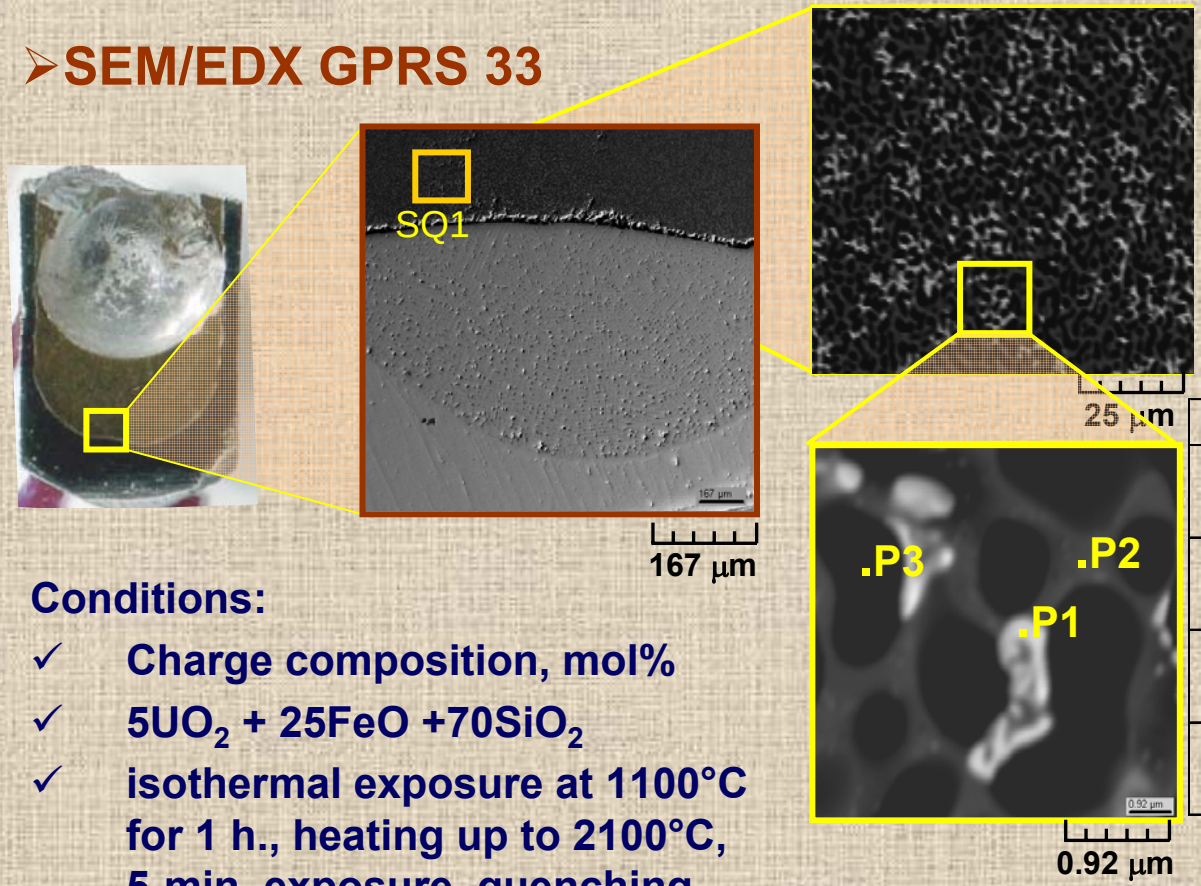


Test	Content, mol.%			Tempera-ture, °C	Exposure time, min	Note
	UO_2	SiO_2	FeO			
GPRS33	5.0	70.0	25.0	1100	60	Annealing
				2100	5	Melting and quenching
GPRS34	10.0	80.0	10.0	1100	60	Annealing
				1850	5	Melting and quenching
GPRS35	20.0	73.0	7.0	1100	60	Annealing
				1950	5	Melting and quenching
GPRS36	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, molybdenum crucibles ∅ 6 mm

UO_2-FeO-SiO_2 system:GPRS #33-36 test results(6)

➢SEM/EDX GPRS 33



#		UO_2	FeO	SiO_2
SQ1	mass.%	15.8	21.7	62.5
	mol.%	4.2	21.6	74.3
P1	mass.%	73.6	14.9	11.5
	mol.%	40.6	30.8	28.6
P2	mass.%	18.5	19.9	61.7
	mol.%	5.1	20.2	74.7
P3	mass.%	4.9	15.7	79.5
	mol.%	1.2	14.1	84.7

Conditions:

- ✓ Charge composition, mol%
- ✓ $5UO_2$ + 25FeO +$70SiO_2$
- ✓ isothermal exposure at 1100°C for 1 h., heating up to 2100°C, 5-min. exposure, quenching

✓No macrostratification was found in the oxidic part of the polished section

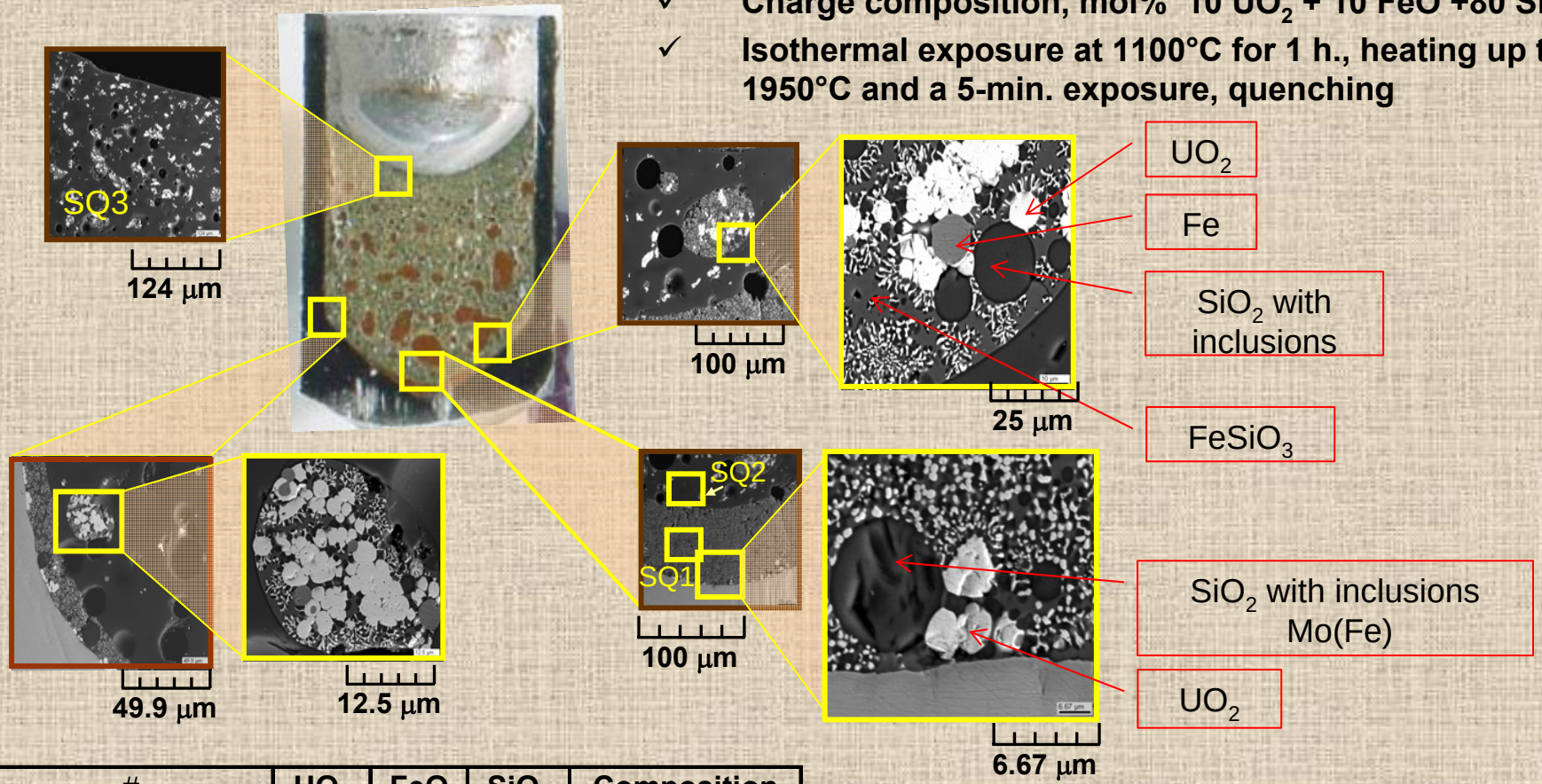
✓Microstructure resembling that of the 'heavy' liquid in the UO_2-SiO_2 system. As a result of the interaction between the melt and the crucible, the composition got depleted in Fe, but no molybdenum was found in the oxidic part

UO_2-FeO-SiO_2 system:GPRS #33-36 test results(7)

➢SEM/EDX GPRS 34

Conditions:

- ✓ Charge composition, mol% 10 UO_2 + 10 FeO +80 SiO_2
- ✓ Isothermal exposure at 1100°C for 1 h., heating up to 1950°C and a 5-min. exposure, quenching

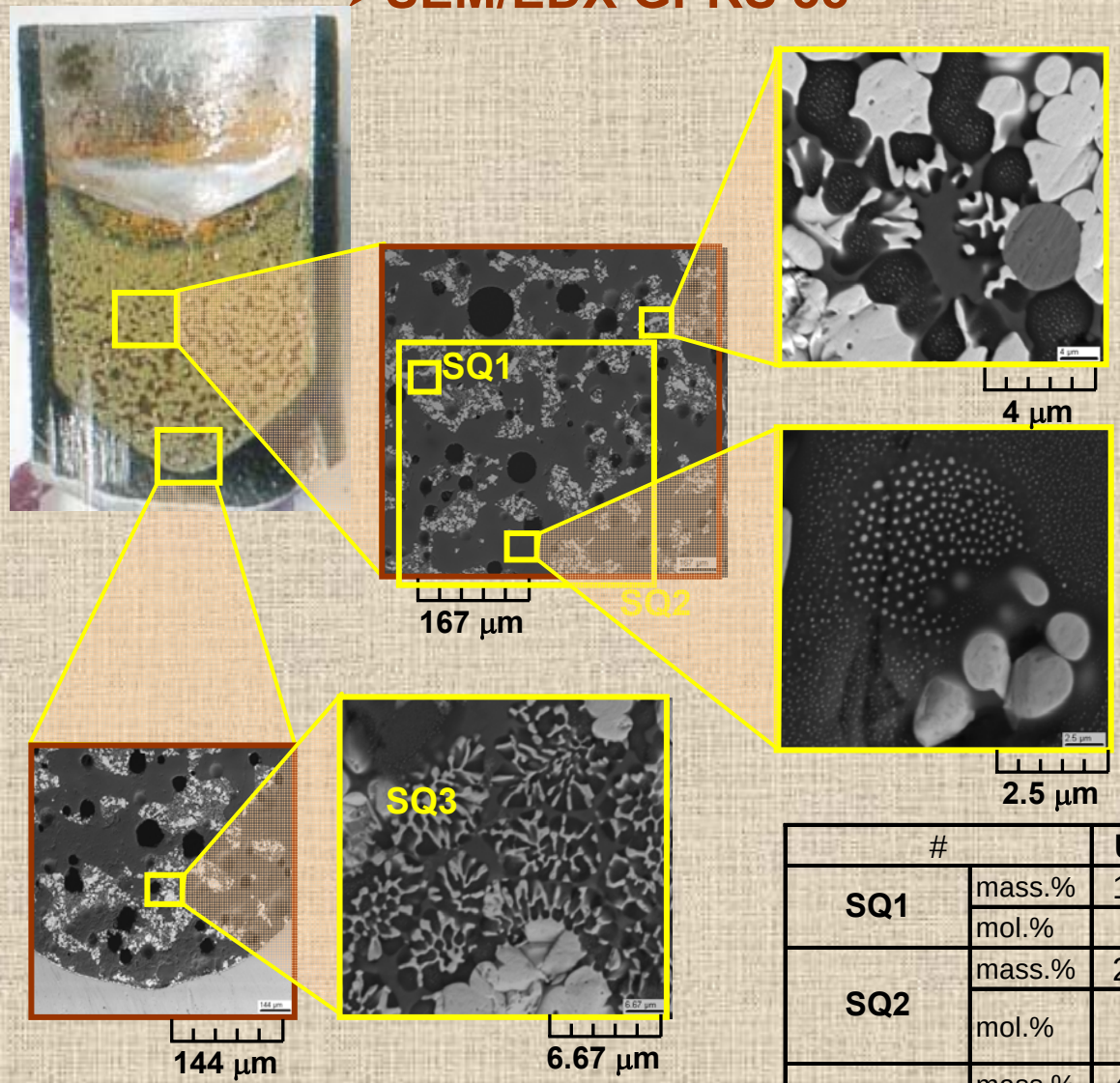


#		UO_2	FeO	SiO_2	Composition
SQ1	mass.%	34.5	19.7	45.8	'Heavy' liquid
	mol.%	11.0	23.6	65.5	
SQ2	mass.%	6.8	3.0	90.3	Light matrix
	mol.%	1.6	2.6	95.8	
SQ3	mass.%	14.5	6.3	79.2	'Light' liquid with globules
	mol.%	3.7	6.0	90.3	

- ✓ Indication of MG
- ✓ The microstructure is nonuniform. Inclusions of irregular shape indicate that the melt exposure time was insufficient (equilibrium was not reached). The globules of heavy liquid contain Fe_{met} drops

UO_2-FeO-SiO_2 system:GPRS #33-36 test results(8)

➢SEM/EDX GPRS 35



Conditions:

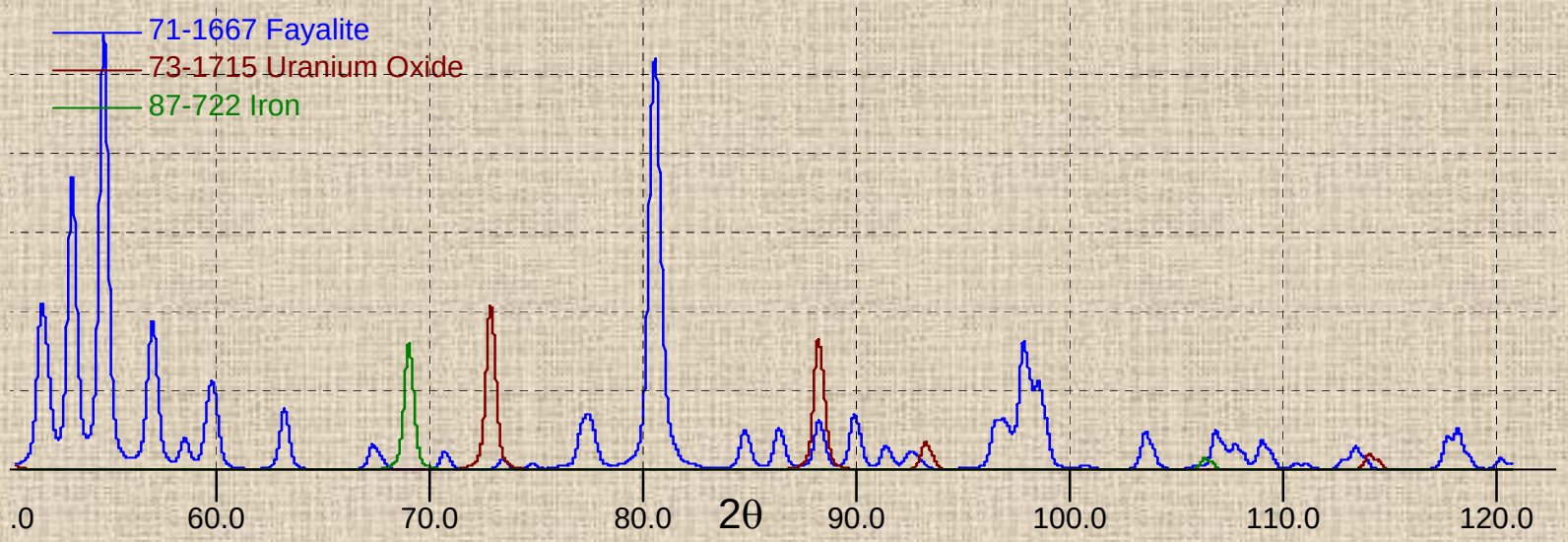
- ✓ Charge composition, mol%
  20 UO_2 + 7 FeO +73 SiO_2
- ✓ Isothermal exposure at 1100°C for 1 h., heating up to 1850°C, 5-min. exposure, quenching

✓Though the macrostructure is uniform, the microstructure is extremely inhomogeneous and resembles that in UO_2-SiO_2 near the binodal

#		UO_2	FeO	SiO_2	Composition
SQ1	mass.%	14.7	3.9	81.4	Light matrix
	mol.%	3.7	3.7	92.6	
SQ2	mass.%	26.6	5.8	67.6	Bulk composition of the total microstructure
	mol.%	7.6	6.2	86.3	
SQ3	mass.%	46.3	11.7	42.0	Globules in the light matrix
	mol.%	16.6	15.8	67.6	

UO_2-FeO-SiO_2 system:GPRS #33-36 test results (9)

✓XRD of sample of GPRS 36 test

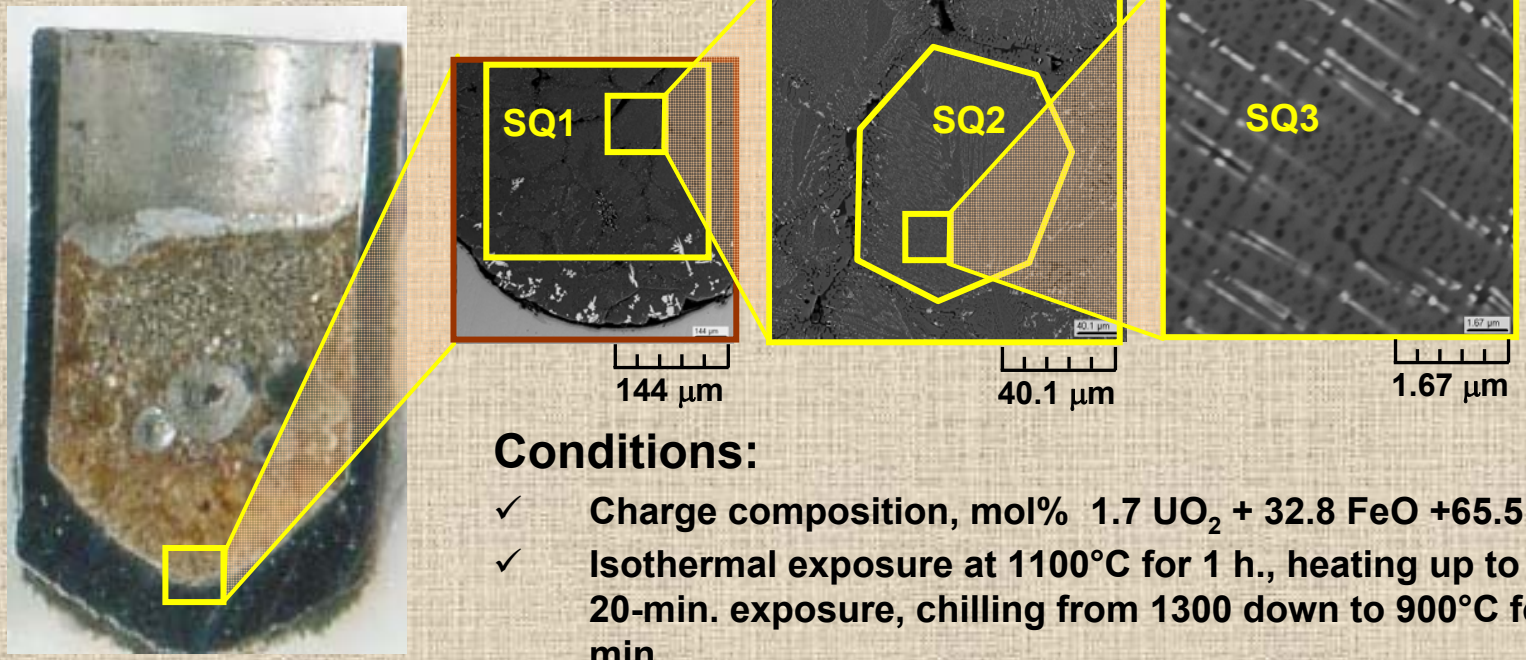


✓The analysis was done using FARAD desktop diffractometer with $CrK\alpha_1$ radiation (λ = 0.22897 nm)

	A Fayalite	B Uranium oxide	C Iron
Formula	Fe_2SiO_4	UO_2	Fe
Card number	71-1667	73-1715	87-722
Phases qualitative ratio	0.052217	0.83252	0.115263

UO_2-FeO-SiO_2 system:GPRS #33-36 test results(10)

➢SEM/EDX GPRS 36



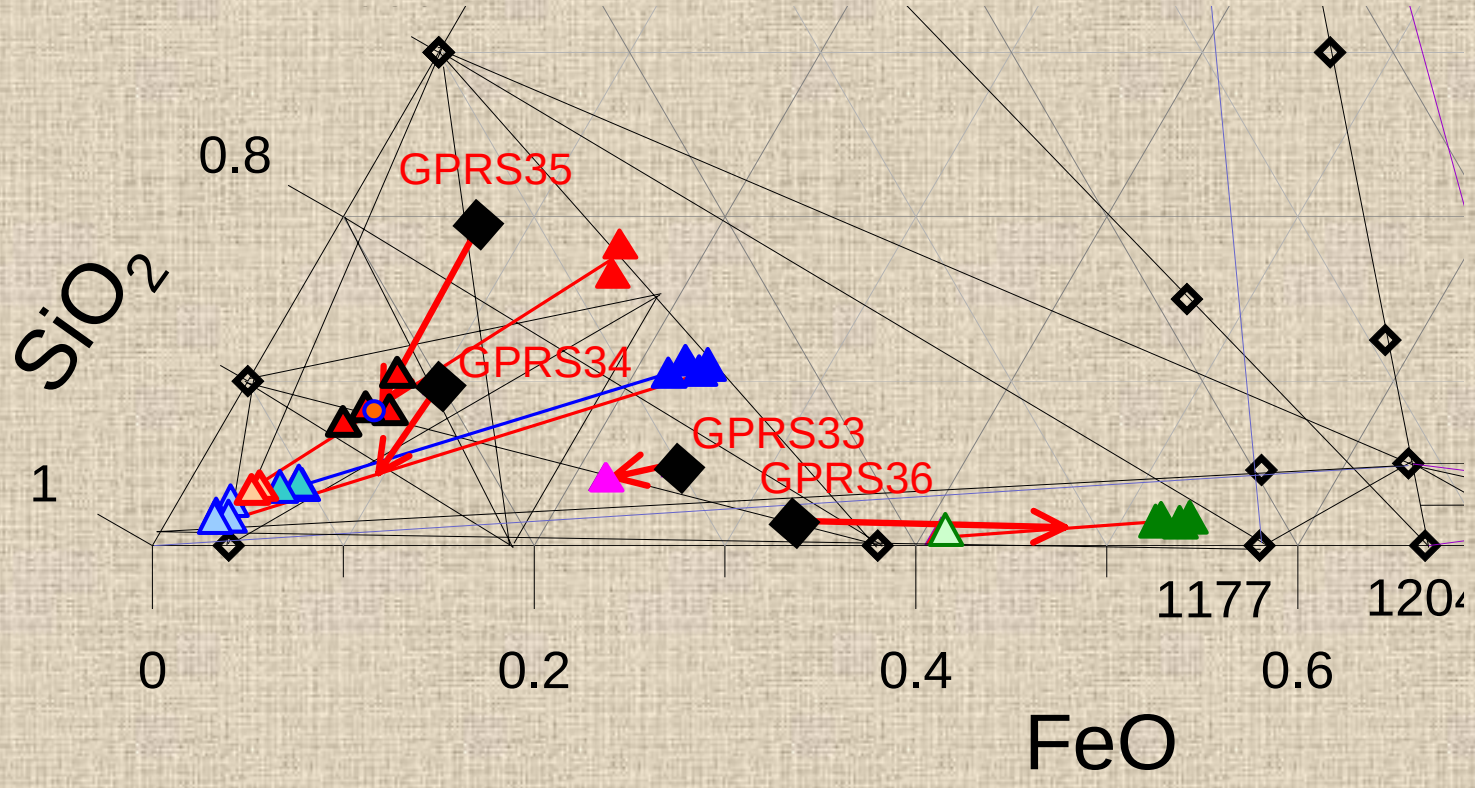
Conditions:

- ✓ Charge composition, mol% 1.7 UO_2 + 32.8 FeO +65.5 SiO_2
- ✓ Isothermal exposure at 1100°C for 1 h., heating up to 1300°C, 20-min. exposure, chilling from 1300 down to 900°C for 240 min.

#		UO_2	FeO	SiO_2	
SQ2	mass.%	5.3	55.2	39.5	Ternary eutectics
	mol.%	1.4	53.1	45.5	
SQ3	mass.%	5.9	53.6	40.5	
	mol.%	1.5	51.8	46.7	

✓Microstructure in the lower part of the crucible shows the eutectic crystallization. In terms of composition, this eutectics lies within a specific triangle UO_2-Fe_2SiO_4-SiO_2.

UO_2-FeO-SiO_2 system: GPRS #33-36 test results(11)



- Characteristic points of the diagram
- Initial composition of the charge
- Bulk composition in GPRS 33 (no MG)
- 'Heavy' liquid in GPRS 34 (T from Tq up to Tm)
- Composition of the 'light' liquid with globules in GPRS 34 (T~Tq~1850C)
- Composition of the light matrix in GPRS 34 (T~Tm)
- Bulk composition of the total microstructure in GPRS 35
- Composition of the liquid at T~Tq~1950C (above MG)
- Light matrix composition in GPRS 35 (T is presumably around Tm)
- Composition of globules in the light matrix in GPRS 35 (T is presumably around Tm)
- Ternary eutectics composition in GPRS 36
- Solid phase composition in GPRS 36

UO_2-FeO-SiO_2 system: test results (12)

- ✓ The performed tests confirm the existence of a miscibility gap in a fairly narrow region adjacent to the diagram corner on the SiO_2 side
- ✓ The ternary eutectics has been determined within a particular triangle of the UO_2 - Fe_2SiO_4 - SiO_2 ternary system
- ✓ The PRS13 test has been performed for determining composition of the second ternary eutectics within a particular triangle of the UO_2 - Fe_2SiO_4 - FeO ternary system. The ingot analysis is underway

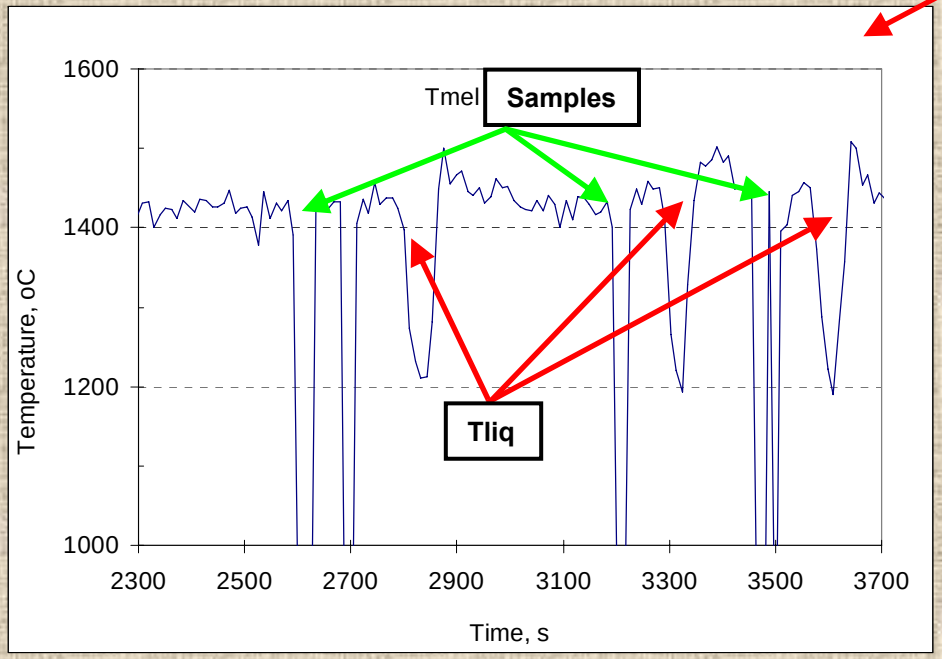
UO_2 – FeO – CaO system: PRS 14 test results

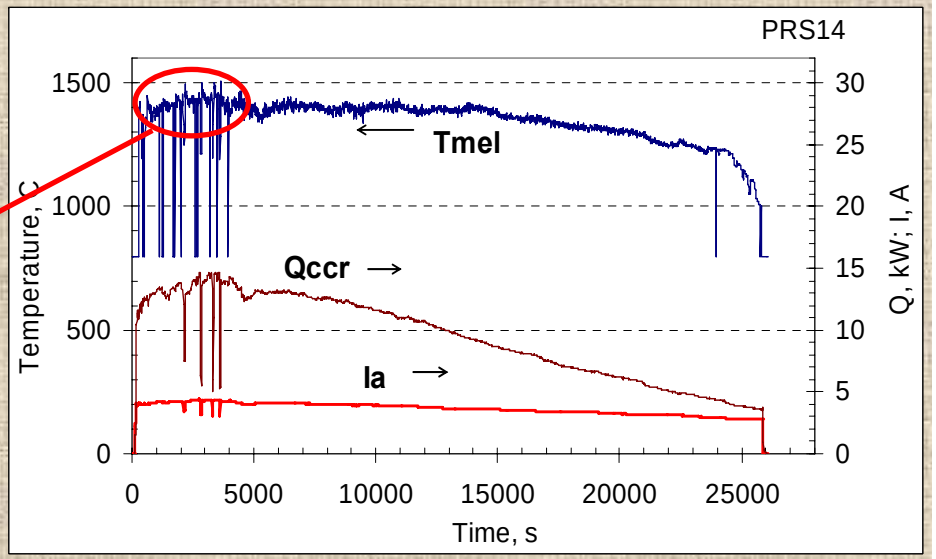
➢Experimental objectives

- T_{liq} determination by VPA IMCC
- Determination of eutectic composition

➢Charge composition

mol.% 20.1UO_2 + 66.7FeO +13.2CaO



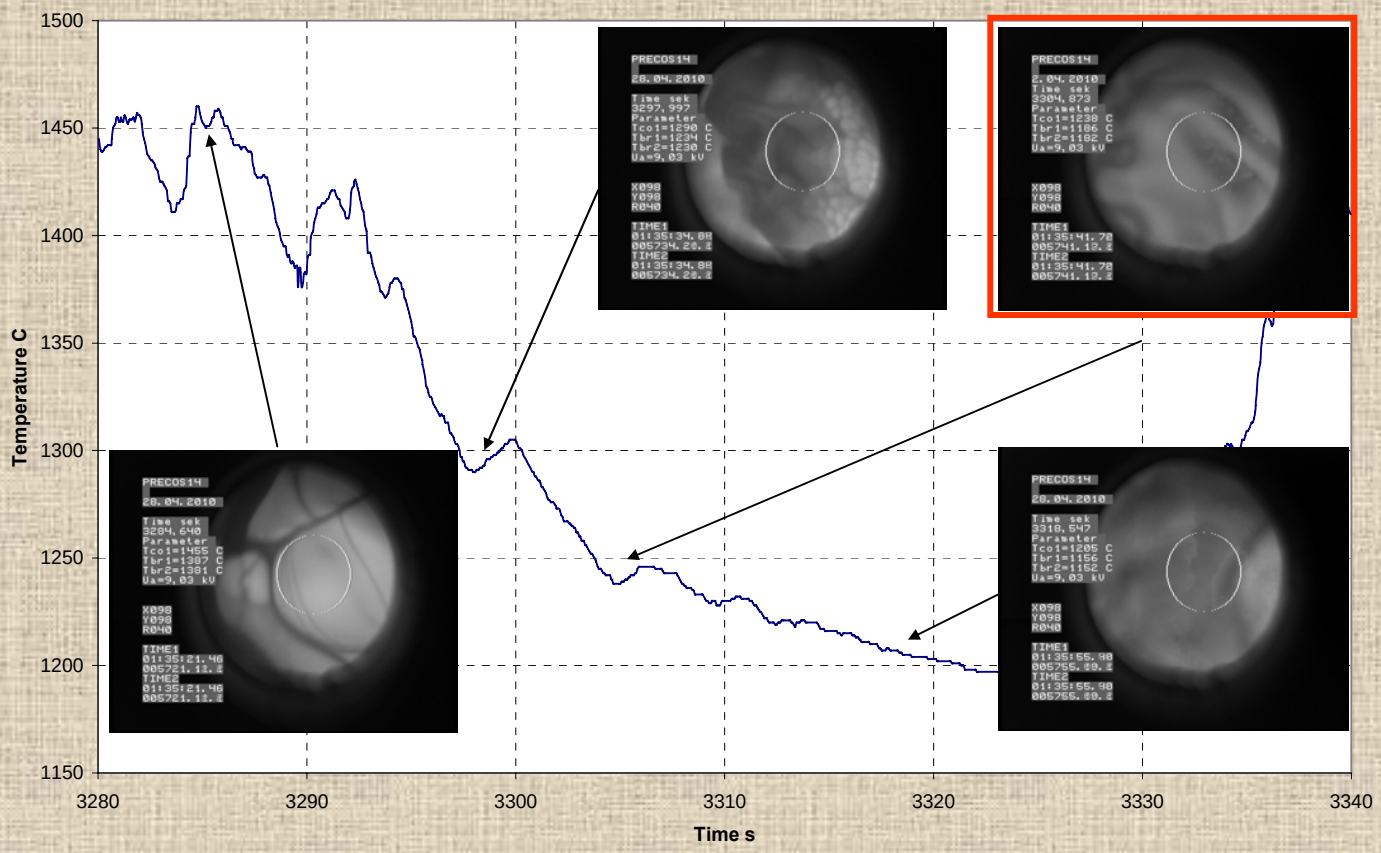


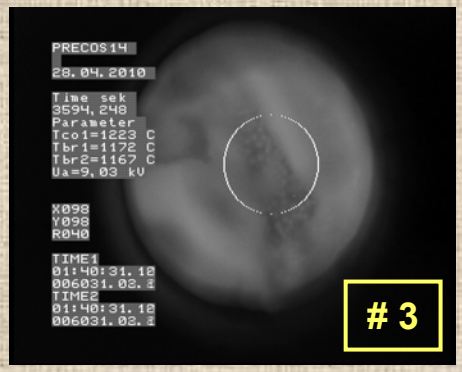
From 4519 s, the pool was pulled out from the inductor at 9 mm/h for 5.9 hours. This has ensured close to equilibrium crystallization and the eutectic liquid displacement into the ingot upper part

✓T_{liq},was measured by VPA IMCC 3 times; video record of one measurement could not be deciphered. Samples were taken 3 times

UO_2 – FeO – CaO system: PRS 14 test results (2)

➢VPA IMCC: Example of thermogram #2 showing melt surface





✓ Results of T_{liq} measurements: 1238, 1247°C

UO_2 – FeO – CaO system: PRS 14 test results (3)

➢XRF and Chemical analysis of melt samples

Samples	Composition mass % / mol.%						T_{liq} °C
	XRF			Cha			
	UO_2	FeO	CaO	UO_2	FeO	CaO*	
2	19.27 / 5.71	66.52 / 74.03	14.22 / 20.27	16.74 / 4.83	66.90 / 72.47	16.36 / 22.70	1238±20
3	19.32 / 5.73	66.74 / 74.38	13.94 / 19.90	18.08 / 5.26	65.01 / 71.06	16.91 / 23.68	1247±20
Charge compo-sition	20.10 / 6.00	66.70 / 75.00	13.20 / 19.00				

* - determined from residue

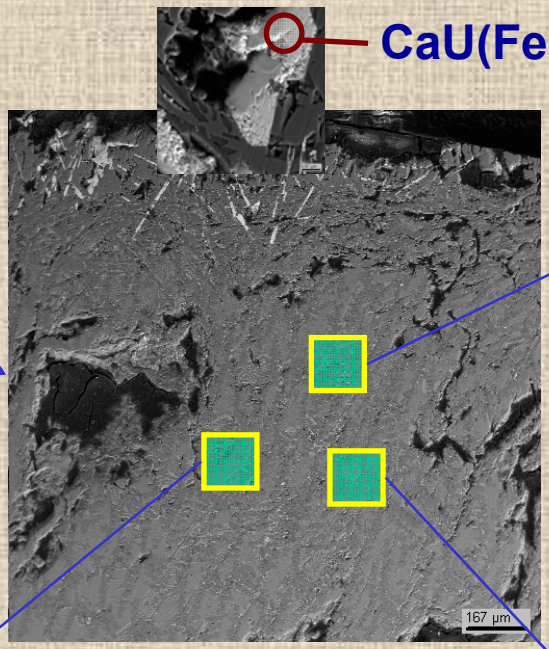
- ✓The results of corium samples XRF and chemical analysis were found to differ significantly
- ✓XRF results are believed to be more accurate, since the content of CaO was not determined by chemical analysis, but calculated from the residue
- ✓ In progress:
  - the SEM/EDX analysis of melt samples

UO_2 – FeO – CaO system: PRS 14 test results (4)

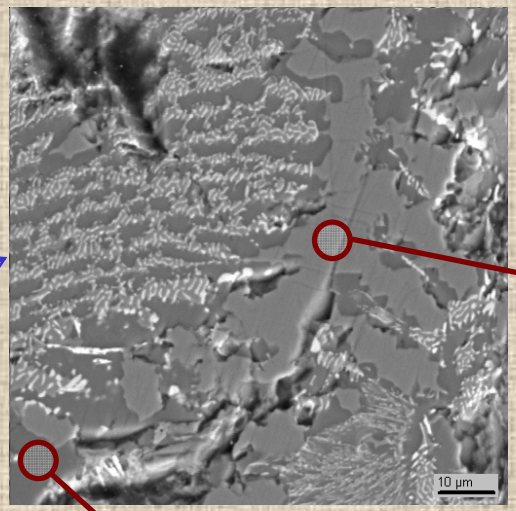
➢SEM/EDX

ingot

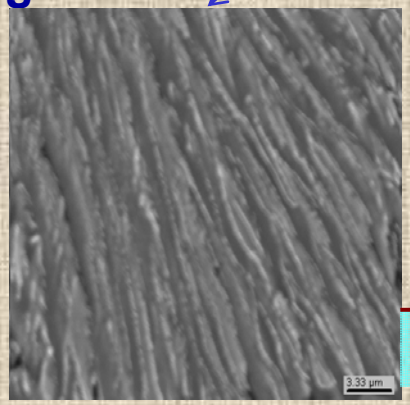
1 sm



250 µm

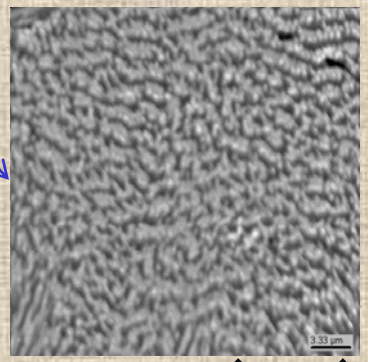


15 µm



6 µm

Eutectic		UO_2	FeO	CaO
EDX	mass %	10.3	62.4	27.2
	mol%	2.8	62.4	34.9



6 µm

Eutectic		UO_2	FeO	CaO
EDX	mass %	10.5	61.4	28.2
	mol%	2.8	61.2	36.0

UO_2 – FeO – CaO system: PRS 14 test results (5)

- ✓ VPA IMCC is used to determine liquidus temperature of composition, mass%:
  19.3±1.0 UO_2 + 66.6±3.3 FeO + 14.1±0.7 CaO –
  T_{liq}= 1242±20 °C

- ✓EDX method is used to determine the ternary eutectic composition, mass%:
  10.4±0.1 UO2 + 61.9±0.5 FeO + 27.7±0.5 CaO

Joint publication with collaborators within the reported quarters

Almjashev V.I., Barrachin M., Bechta S.V., Bottomley D., Defoort F., Fischer M., Gusarov V.V., Hellmann S., Khabensky V.B., Krushinov E.V., Lopukh D.B., Mezentseva L.P., Miassoedov A., Petrov Yu.B., Vitol S.A.

Phase equilibria in the FeO_{1+x}–UO_2–ZrO_2 system in the FeO_{1+x}-enriched domain
// JNM. 2010. V. 400. N. 2. P. 119–126

3rd PRECOS project meeting

(June 2, 2010, St. Petersburg)

Objectives:

- Discuss test results related to binary and ternary oxidic systems:

  UO_2-SiO_2; UO_2-CaO; ZrO_2-FeO_y

  UO_2-FeO-SiO_2; UO_2-FeO-CaO

- Discuss and agree upon future works
- Discuss possible reasons of discrepancies between XRF, Chemical and EDX analyses of UO_2-SiO_2 and UO_2-CaO samples
- Publications
- To discuss PRECOS project prolongation without additional funding

3rd project meeting decisions about further work

- Conduct 1 experiment in the UO_2-SiO_2 system by LPH method
- Cancel the studies of eutectic points in the ZrO_2–FeO–SiO_2, ZrO_2–FeO–CaO systems for a more detailed study of priority system
- Check melt pollution by the crucible material in the GPRS experiments in the UO_2-FeO-SiO_2 system, to determine a possibility of studies in the Mo crucibles and discuss it with collaborators

Concluding remarks

- ✓ Experimental studies in the UO_2-CaO system have been completed
- ✓ Study of the UO_2-CaO-FeO ternary system have been started
- ✓ Plans for quarters # 10 - 11:

- Complete the UO_2-CaO systems and start a report preparation

- Continue study of the ZrO_2-FeO_y ; UO_2-SiO_2-FeO; CaO-UO_2-FeO and U-Zr-O systems (the last one by LPH in IVT RAN)