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Annual progress report

PROJECT № 1950.2-2003

PHASE DIAGRAMS FOR MULTICOMPONENT SYSTEMS CONTAINING CORIUM AND PRODUCTS OF ITS INTERACTION WITH NPP MATERIALS

(CORPHAD 2)

Phase 2. First year

(01.07.2003 – 30.06.2004)

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Annual report
Project № 1950.2-2003

1. Project title	Phase diagrams for multicomponent systems containing corium and products of its interaction with NPP materials (CORPHAD)
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5. Date of project start	01 July, 2003
Project duration	36 months

6. Project goal and expected results

Main project goal is to enhance the safety of VVER, PWR and BWR reactors in case of a severe accident involving core meltdown. Specific project objective is to make an experimental identification of phase diagrams of multi-component corium systems and products of its interaction with NPP construction and structural materials.

Among the measures ensuring VVER, PWR and BWR safety under severe accident conditions is the stabilization of molten core within the containment and reduction of gaseous and solid fission product releases beyond the containment down to the safe level.

At present the following two accident management strategies are accepted for operating and developed NPPs with VVER, PWR and BWR reactors:

- the in-vessel melt retention accompanied by the passive external vessel cooling with boiling water - mostly for medium capacity reactors.
- ex-vessel core catchers for corium retention - for higher-capacity reactors.

Knowledge about phase diagrams of coria having a wide range of compositions is necessary for numeric modeling of phenomena taking place at the interaction of molten corium with construction and structural materials of reactor unit, concrete pit and core catcher. This knowledge is necessary for the core catcher availability analysis. The phase diagram calculations of multi-component systems are performed using thermodynamic computer codes and code-oriented databases, which have been compiled on the basis of experimental measurements.

The present-day inventory of experimental data on phase diagrams of systems containing uranium-bearing corium is insufficient, which is explained by the following factors:

- complexity of an experimental examination of a high-temperature (up to 3300 K) reactive corium, which can be performed at just a few currently available test facilities;
- new construction and structural materials used in newly-developed VVER, PWR and BWR-based NPPs; also a new class of sacrificial materials proposed for a severe accident management;
- newly-found phenomena accompanying the in-and ex-vessel stages of severe accident development, which influence the molten pool structure and characteristics, e.g. U and Zr extraction by molten steel from suboxidized melt;
- national regulatory restrictions on handling uranium-bearing systems.

CORPHAD is the project aimed at getting additional experimental data, the absence of which is explained by the above-listed factors. The project implementation will provide the essential experimental data on phase diagrams of binary, ternary, quaternary and prototype multi-component systems for the numeric code refining and database optimization. The data will cover suboxidized U – Zr – Fe – O systems with a miscibility gap. The following basic characteristics will be experimentally determined:

- concentration curves of solidus and liquidus temperatures;
- coordinates of characteristic points: eutectics, dystectics and others;
- component solubility limits in the solid phase;
- temperature – concentration regions of the miscibility gap.

The project results will be used for:

- addition of previously absent or specified experimental data on phase diagrams of oxidic and metal-oxide corium systems to databases;
- numeric model specification, especially in terms of modeling the miscibility gap and quasi-equilibrium states in thermal gradient conditions;
- verification of thermodynamic numeric codes, which model phase diagrams of multi-component systems resulting from the interaction of the molten core with construction and structural materials of reactor, concrete pit and core catcher;
- safety analysis and enhancement of operating and new NPPs having VVER, PWR and BWR reactors.

7. Experimental approach

CORPHAD tests are performed on "Rasplav-2" and "Rasplav-3" tests facilities, which provide conditions for experimental studies with realistic coria heated up to 3300 K. "Rasplav-2" is used for tests with oxidized and suboxidized oxidic systems; "Rasplav-3" – for tests with metal-oxide systems. The method of induction melting in a cold crucible (IMCC) is used for producing corium melt. The methods is quite suitable for phase diagram studies (it is the only technique suitable for studying certain systems), because the presence of a solid phase (crust) between the melt and cold crucible prevents the mass transfer of crucible materials into the melt, ensures the melt retention in the crucible and a high purity of the melt (at the degree of initial components). The IMCC provides contact-free heat transfer and deposition in the melt. "Rasplav-2" and "Rasplav-3" are capable of producing up to 8 and 2 kg of high-temperature melt respectively in the inert, air and steam atmosphere.

For certain experimental studies the following installations are used additionally: Galakhov microfurnace, high-temperature microscope, derivatographs, high-temperature differential thermoanalyzer, cold crucible, "Tighel" installations with ohmic graphite heater-crucible with inside plating of metallic zirconium. These optionally-used test facilities belong to the Institute of Silicate Chemistry of the Russian Academy of Sciences (ISCh RAS), St. Petersburg State Electrotechnical University (SPb SEU) and RRC Kourchatov Institute (RRC KI). These installations provide conditions for studying phase diagrams under temperatures up to 2800 K and getting adequate and reliable experimental data.

Therefore, this experimental complex as a whole enables to employ the following experimental techniques for phase diagram studies:

- Visual polythermal analysis (VPA);
- Visual polythermal analysis in the cold crucible (VPA IMCC);
- Differential thermal analysis (DTA) and differential scanning calorimetry (DSC);
- Thermal analysis;
- Galakhov microfurnace (GM);
- High-temperature microscopy (HTM).

These methods have been tested and produced reliable results during the implementation of METCOR, CIRMAT, CIT, ENTHALPY, ECOSTAR, OESD/MASCA projects.

The following methods have been used for physico-chemical analysis:

1. Analysis of elemental composition

- X-ray fluorescence analysis (XRF);

- Chemical analysis (ChA);
- Mass-spectrometry with inductively-coupled plasma (ICP MS);
- Spark source mass spectrometry (SS MS).

2. Phase composition analysis

- X-ray diffractometry (XRD).
- Energy dispersion X-ray (EDX);

3. Metallo- and ceramography (Opt M).

- Optical microscopy;
- Scanning electron microscopy (SEM).

During the preparatory period and in the course of the 1st year of project implementation some installations were modernized and phase diagram investigation methods improved (e.g. VPA IMCC, Galakhov microfurnace, etc); the methodologies for physico-chemical analysis of uranium-bearing corium samples have been refined.

8. Project implementation progress and main results

In accordance with CORPHAD-2 Work Plan and its updates recorded in Minutes №2 and №3 of CORPHAD-2 Steering Committee meetings, which were held on September 17, 2003 in St. Petersburg (Russia) and February 9, 2004 in Paris (France), the subject of the 1st year experimental studies was: "Phase diagrams of binary oxidic systems" (Task 1): UO_2 - FeO, ZrO_2 - FeO, SiO_2 - Fe_2O_3 (Fe_3O_4), SiO_2 - Fe_3O_4. In accordance with the decision of the 2nd and 3rd Steering Committee meetings (Minutes №2 and №3) binary systems $UO_{2\pm x}$ - FeO_y, UO_2 - Cr_2O_3 and (BaO, SrO) - UO_2 were excluded from Task 1 experimental matrix as having low and medium priority. It was decided to study higher-priority systems in more detail.

A decision about the studies of the UO_2 - SiO_2 phase diagram will be taken after the analysis of available data on them and the data credibility check.

In accordance with the experimental matrix of Task 2 the following phase diagram studies of ternary systems have been performed: U – O – Fe (in progress); and $UO_{2\pm x}$ - ZrO_2 - FeO_y eutectics composition and temperature (has been started).

Man results of completed studies are presented below.

8.1 Studies of binary systems. UO_2 - FeO.

The interaction of uranium oxide and iron monoxide is one of the processes taking place inside the reactor vessel during a severe accident involving the core meltdown. The UO_2 – FeO phase diagram were partially studied within the EU CIT project; then only eutectics point parameters and liquidus temperature in the low-temperature domain of the phase diagram were determined.

Therefore, the current study had the following objectives:

- to determine liquidus and solidus temperatures in the wide range of UO_2 – FeO compositions in the inert atmosphere;
- to specify eutectics composition and temperature;
- to determine the final solubility of FeO in UO_2.

11 tests have been conducted, their specifications, initial charge compositions and experimental objectives are given in Table 1.

Table 1

The investigation of UO_2 – FeO system

Test #	Charge composition, mass. %				Mass of furnace charge, g	Experimental objective
	UO_2	FeO	Fe	Fe, getter.		
CORD 6	39.28	54.38	5.35	0.99	173	T_{liq} determination
CORD 7	59.08	36.35	3.58		203	
CORD 8	11.16	80.02	7.83		154	Ingot extraction. Eutectics determination
CORD 14	16.26	76.27	7.47	-	156	
CORD 17	39.50	53.88	5.63	0.99	375	T_{liq} determination
CORD 18	59.30	35.94	3.77		420	
CORD 19	49.25	45.31	4.44		396	
CORD 20	16.17	75.01	7.83		334	Ingot extraction. Eutectics determination.
CORD 21	79.13	18.0	1.88		470	T_{liq} determination
CORD 22	89.02	9.1	0.89		495	
CORD 23	69.20	26.98	2.83		440	

All tests were performed in argon. In order to produce FeO the metallic (carbonyl) iron was introduced into the charge, to render FeO stoichiometric a carbonyl iron getter was added into the melt. Tests CORD 6, 7, 8 were performed at "Rasplav-2", the rest - at "Rasplav-3" facility.

The following methods were used for measuring liquidus, solidus and eutectics temperatures:

- The VPA IMCC was used for determining liquidus and eutectics temperature for eutectic composition. In tests CORD 8, 14, 20 the synthesis of eutectic composition was performed by melt crystallization in close-to-equilibrium conditions, which was achieved by slow (5 – 10 mm/h) crucible shift vs. inductor; it was followed by the posttest analysis of samples from the ingot part, where the last liquid phase got crystallized. The DTA of eutectics sample was also performed. The VPA IMCC method was modified by introducing water-cooled electromagnetic screen into the crucible top zone, which enabled to cool only the molten pool surface layer without changing the melt bulk temperature and, consequently, its composition.
- Liquidus and solidus temperatures were measured by VPA in the Galakhov micro-furnace, the quenched samples of melt and ingot were used for these measurements.
- Solidus temperature was measured by DTA on the SETSYS Evolution – 2400 analyzer, the operational temperature range of which is 196 - 2400 °C. Solidus temperature was derived from the start of exothermal effect during the heating of quenched melt and ingot samples.

Chemical analysis of samples and ingots was performed for confirming the stoichiometry of initial oxides during the test and for determining the melt composition during the liquidus (eutectics) temperature measurements.

The ingot microstructure, elemental and phase composition was determined by SEM and EDX analyses.

Appendix 1 presents the experimental studies of UO_2 – FeO phase diagram in detail. Only main results are reviewed in this section.

The position of eutectics point was determined in tests CORD 8, 14, 20 using VPA IMCC, VPA in the Galakhov microfurnace and DTA.

At this:

- T_{eut} = 1342 °C (in accordance with CIT data T_{eut} = 1340 °C)
- Eutectics composition: 86.4 mass. % FeO and 13.6 mass. % UO_2 (in accordance with CIT data eutectics composition 88.6 mass. % FeO and 11.4 mass. % UO_2)

Liquidus temperatures of the UO_2 – FeO system have been determined. The results of T_{liq} studies by the VPA IMCC are given in Table 2. Table 3 presents T_{liq} determined by VPA in the Galakhov microfurnace.

Table 2

Liquidus temperature of the UO_2 – FeO system determined by VPA IMCC

CORD #	FeO content in the melt, mass.%	Liquidus temperature T_{liq}, °C
17	67.63	1580
18	48.49	1802
19	58.23	1694
20		1370
21	23.76	2147
22	11.36	2368
23	34.21	1959

Table 3

Liquidus temperature in the UO_2 – FeO system determined by VPA in the Galakhov microfurnace

CORD #	FeO concentration in the melt, mass.%	Liquidus temperature T_{liq}, °C
17	73.22-87.62	1456-1470
18	57.81-66.86	1515-1520
19	66.79-77.79	1560-1625
21	89.45	2020
23	45.89-47.	1815

The final solubility of FeO in UO_2 was determined, which at 1342 °C was ≈ 5.08 mass.% FeO.

8.2 Studies of binary systems. ZrO_2 - FeO

The ZrO_2 – FeO phase diagram is of great practical value, because under severe accident conditions with core meltdown this system undergoes phase transformations in the partially oxidized molten corium. This binary system is the basis for a more general ternary system Zr – Fe – O, which will be examined within the CORPHAD-2 project as well. Phase equilibria in the ZrO_2 – FeO system were examined in [1], which determined the eutectics point composition and

temperature, solid solution region in the low-temperature area (at high concentrations of FeO) and a phase diagram in the temperature range limited by 1700 °C. Therefore, the high-temperature part of the diagram near ZrO_2 has remained unstudied.

Objectives of the current investigation were as follows:

- to determine liquidus and solidus temperatures in the wide range of ZrO_2 – FeO compositions during melting in the inert atmosphere;
- to check and specify eutectics composition and temperature determined in [1];
- to determine the final solubility of FeO in ZrO_2 having different crystalline modifications.

14 tests have been performed, their list is given in Table 4, which also provides data on initial charge compositions and experimental objectives. The melting sessions were conducted under inert atmosphere and reducing conditions in the melt, so that FeO could be maintained as a melt component. This last condition was achieved by introducing a getter, metallic iron, into the melt.

Table 4

Tests on ZrO_2 – FeO studies

Test #	Initial charge, mass.%		Experimental objective
	ZrO_2	FeO	
CORD 1,2	3	97	T_{eut} determination
CORD 3,4	50	50	T_{liq}, T_{eut}
CORD 5	70	30	T_{liq}, T_{eut}
CORD 9	16,4	83,6	T_{eut}
CORD 10	50	50	T_{liq}
CORD 11	35	65	T_{liq}
CORD 12	35	65	T_{liq}
CORD 13	25	75	T_{liq}
CORD 15	60	40	T_{liq}
CORD 16	80	20	T_{liq}
CORD 24	65	35	T_{liq}
CORD 29A	95	5	$T_{cub>tetr}$

The following methods were used for measuring liquidus and eutectics temperatures:

- visual polythermal analysis in a cold crucible (VPA IMCC)
- visual polythermal analysis in the Galakhov microfurnace (VPA GM)
- differential thermal analysis (DTA).

The melt and ingot samples have been subjected to special methods of physico-chemical analysis, which produced the data on:

[1] W.A. Fischer, A. Hoffman, Archiv Eisenhüettenw.,28, №739,1957

- elemental composition (chemical analysis, XRF and SEM/EDX analysis);
- phase composition (XRD and SEM/EDX analysis);
- microstructure (SEM/EDX analysis).

A detailed description of the ZrO_2 – FeO phase diagram studies is given in Appendix 2. This section presents the main results.

The position of eutectics point has been determined. Tests CORD 2,4,5,9 have produced the following results:

- $T_{eut} \approx 1330$ °C (data of [1]: $T_{eut} = 1330 \pm 15$ °C)

- Eutectics composition 83,6 mass. % FeO and 16,4 mass. % ZrO_2 (data [1]: 97 mass. % FeO and 3 mass. % ZrO_2)

Liquidus temperatures of refractory compositions have been determined. Table 5 presents experimental results.

Table 5

Liquidus temperature of the ZrO_2 – FeO system determined by VPA IMCC

CORD #	**FeO content in the melt, mass.%**	**Liquidus temperature T_{liq}, °C**
13	77.45	1696
12	68.17	1793
4	54	2030
10	53.41	2020
24	41.6	2112
15	39.81	2161
5	31	2295
16	15.53	2400

Table 5 shows the melt compositions determined by the chemical analysis and XRF of the melt samples.

T_{liq} values determined by the VPA IMCC can be lower than actual (up to 30÷40 °C) due to the molten pool dynamics and its vertical thermal gradient.

The following parameters of ZrO_2-based solid solutions have been determined:

– the cubic solid solution has the final FeO concentration ≈ 7 mass.% under 1800 °C and is stable under 2700 ÷ 1800°C;

– tetragonal solid solution has the final FeO concentration of 1,3 mass.% under 1330 °C and remains stable under 2347 ÷ 1172 °C.

The experimental data enabled to construct the phase diagram of ZrO_2 – FeO system, which was determined as a simple eutectics having a region of final solid solutions based on several ZrO_2 modifications.

8.3 Studies of binary systems. Fe_2O_3 (Fe_3O_4) – SiO_2 и Fe_3O_4 - SiO_2

Phase diagrams of Fe_2O_3 (Fe_3O_4) – SiO_2 are of great practical interest, because at the ex-vessel stage of a severe accident the relocated molten corium may contain a considerable concentration of iron oxides (steel oxidation products and components of the core catcher sacrificial material) and molten silicon oxides resulting from the interaction of corium with concrete, sacrificial and refractory materials. At this stage melts are subjected to a long-term exposure to oxidizing conditions, i.e. the steam-gas atmosphere.

Up to now the reliable data on Fe_2O_3(Fe_3O_4) – SiO_2 phase diagrams has not been found in publications. The most detailed of available studies is [2] on the ternary FeO-Fe_2O_3-SiO_2 system. But this study practically does not consider the region at the triangle top, which corresponds to Fe_2O_3, and does not examine phase equilibria in the Fe_2O_3 - SiO_2 and Fe_3O_4 - SiO_2 systems.

Objectives of the current study were formulated in the following way:

- to determine liquidus and solidus temperatures of the Fe_2O_3 - SiO_2 system in air and in flowing oxygen;
- to determine liquidus and solidus temperatures of the Fe_3O_4 - SiO_2 system in the inert atmosphere;
- to determine eutectics composition and temperature in the Fe_2O_3 - SiO_2 and Fe_3O_4 - SiO_2 systems.

The following methods have been used for the studies: DTA, VPA with the Galakhov microfurnace and high-temperature microscope (HTM). The microstructure and elemental composition of specimens after melting in the Galakhov microfurnace and HTM was determined by SEM/EDX analysis.

The substances used for the Fe_2O_3 - SiO_2 studies were high-purity oxides – 99.97% Fe_2O_3 and 99.99% SiO_2 (Brazilian rock crystal).

The substances used for the Fe_3O_4 - SiO_2 studies were magnetite (FeO Fe_2O_3) and high-purity silica. Magnetite used as a precursor was produced by the 1-hour exposure of initial substance to 1300 °C in argon following the reaction:

$Fe_2O_3 + Fe \rightarrow Fe_3O_4$,

where Fe – carbonyl iron.

The experimental examination of the Fe_2O_3 - SiO_2 and Fe_3O_4 - SiO_2 phase diagrams is presented in more detail in Appendix 3. This section provides an overview of main results.

The Fe_2O_3 (Fe_3O_4) – SiO_2 system

Solidus and liquidus temperatures were measured in air and in flowing oxygen, the partial pressure of oxygen was 0.21 and 1 atm. respectively. The Fe_2O_3 – SiO_2 system has been found to contain magnetite (Fe_3O_4) as an additional component under temperatures higher than the temperature of Fe_2O_3 decomposition to Fe_3O_4 (1375 and 1430 C in air and oxygen respectively). Due to the incomplete decomposition the system is shown as Fe_2O_3 (Fe_3O_4)– SiO_2.

Solidus and liquidus measurements of the Fe_2O_3 – SiO_2 specimens in flowing oxygen and in air gave similar values, which are shown in Table 6.

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[2] Muan A., Osborm E.F. Phase equilibria at liquidus temperature in the system MgO- FeO-Fe_2O_3 - SiO_2// J.Am.Ceram.Soc1956.v.39, N 4, p.121-140

Table 6

Fe_2O_3 (Fe_3O_4) – SiO_2 solidus and liquidus composition and temperature

Composition, mass.%		Temperature, °C		
Fe_2O_3	**SiO_2**	**solidus**	**liquidus**	**monotectics**
100	0		1539	
96	4	1470	1517	
93	7	1470	1505	
92	8	1470	1490	
89	11	1470	1470	
88	12	-	1475	
87	13	1470	1490	
86	14	1470	1505	
80	20	1470	-	1539
73	27		-	1530
73	27		-	1530
64	36		1736	1530
40	60		1761	1530
23	77		1736	-
21	79		1640	1538
20	80		-	1538
18	82		1655	-
16	84		1655	1538
14	86		-	1538

The experimentally determined eutectics point corresponds to ≈1470 °C and composition 89 mass. % Fe_2O_3. The liquation region derived from the liquidus curve direction lies within concentrations ranging from ≈78-80 mass. % Fe_2O_3 to ≈20-10 mass. % Fe_2O_3.

The Fe_3O_4 - SiO_2 system

The experimental examination was carried out in the inert atmosphere (argon and helium). Iridium specimen holder was used in the Galakhov microfurnace, which excluded its interaction with the studied specimen.

Table 7 presents the liquidus and solidus measurements of the Fe_3O_4 - SiO_2 system in the Galakhov microfurnace.

Table 7

Fe_3O_4 – SiO_2 composition and liquidus-solidus temperature

Composition, mass.%		Temperature, °C		
Fe_3O_4	**SiO_2**	**solidus**	**liquidus**	**quenching**
97	3	1449	1575±14	-
94	6	-	1560±13	-
90	10	1441	1511	-
85	15	1446	1540	-
79	21	1448	1526	-
88	12	1445	1466±5	1476
72	28	1425	1765±4	1800
62	38	1581	1728±11	1820
49	51	1572	1605±16	1640
30	70	1434±13	1558±2	1620
17	83	1440	1693±12	1780
11	89	-	1685±3	1680
20	80	-	1721±5	2000
95	5	-	1700	1950

A further analysis of the specimens produced during the experiment in the Galakhov microfurnace specified the liquidus curve direction and eutectics point position. The analysis of elemental composition and identification of microstructure were carried out for that.

The integration of SEM/EDX analysis results and Galakhov temperature measurements enabled to construct the specified Fe_3O_4 – SiO_2 diagram, which is shown in Appendix 3. This diagram has one eutectics point at ≈1440 °C and composition 85 mass. % Fe_3O_4. The liquation region lies within the Fe_3O_4 concentrations between 80 - 20 mass. % .

The comparison between phase diagrams of Fe_2O_3 (Fe_3O_4) – SiO_2 and Fe_3O_4 – SiO_2 systems shows that they are close, but not identical due to the incomplete decomposition of Fe_2O_3 to Fe_3O_4, which is reversible.

8.4 Studies of ternary systems. U - Zr – O

The phase diagram of the ternary U - Zr – O system enables to model one of the basic core degradation phenomena taking place under severe accident conditions – the interaction of uranium oxide and zirconium in the atmosphere with oxygen deficit. Until present the experimental complexity of the studies put a barrier to getting comprehensive data on different sections of the ternary diagram depending on the oxygen concentration. Along with that, the extensive data on closely located sections of this phase diagram, which have been produced in [3] and [4], have a considerable divergence.

Therefore the objectives of the current examination were:

- to study liquidus and solidus temperatures for the sections of ternary $ZrO_{0,54}$ –UO_2 and $ZrO_{0,43}$ –UO_2 diagrams, which have been studied in [3] and [4] respectively.

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[3] Hayward P.J., George I. M., J. Nuclear Materials, 232, (1996), p.13

[4] Scocan A., 5th Meeting on Thermal Nuclear Reactor Safety, Karlsruhe, Spt. 9 – 13, (1984)

- To study liquidus and solidus temperatures for other U - Zr – O ternary diagram sections having practical relevance.

By now 5 tests, CD 3,4,5,6,7, have been completed on the “Tighel” test facility of the RSC “Kourchatov Institute”; and 2 tests, CORD 28 and CORD 29 on the "Rasplav-3" test facility. Table 8 presents the test specifications.

Table 8

Specification of the U-Zr-O studies

Test #	Initial charge, at%			Temperature, °C		Note
	U	Zr	O	T_{liq}	T_{sol}	
CD3	13.0	43.0	44	2135	2075	Tests at “Tighel” facility in a graphite crucible with a zirconium carbide film
CD4	8.0	52.0	40.0	2100	2077	— ” — ” —
CD5	16.0	36.0	48.0	2275	2025	— ” — ” —
CD6	23.0	19.0	58.0	2320-2400	-	Tests at “Tighel” facility in a tungsten crucible
CD7	23.0	19.0	58.0	2380	-	Tests in the tungsten crucible: 0.32 mass% of carbon dust was added into the melt
CORD28 1 composition	8.0	52.0	40.0	2085	-	Tests at “Rasplav” facility
CORD28 2 composition	13.0	43.0	44.0	2170	-	— ” — ” —
CORD29	20	17	63	2460	-	— ” — ” —

Experiments CD 3,4,5 were carried out at the “Tighel” tests facility in the ohmic graphite heater-crucible having the 4.5 kW capacity, the inside surface of which was plated with zirconium.

Experiments CD 6,7 were conducted in the tungsten crucibles having 14 mm outer diameter, sidewall thickness 0.4 mm and 1 mm-thick bottom, the crucibles were mounted inside the ohmic graphite heater. In order to reduce the penetration of carbon inside the crucible it was covered with a tantalum foil cover.

In tests CD 3 ÷ 7 liquidus and solidus temperatures were determined by a modified thermal analysis, i.e. the thermogram differentiation at cooling. To ensure the data reliability the melt was heated and cooled several times during one test. Experiments CORD 28, 29 were performed on “Rasplav-3”. The liquidus temperature for two compositions of the system was examined within a single test, CORD 28. After measuring liquidus temperature of the 1st composition (Table 8), additional UO_2 and metallic zirconium pellets were introduced into the melt and liquidus temperature of the second composition was measured (Table. 8).

In CORD 28, 29 the VPA IMCC with electromagnetic screen was used for determining liquidus temperature. The following two methodologies were used for the physico-chemical analysis of the melt samples taken by the rod during liquidus measurements:

- photocalorimetric determination of U (IV) and (VI) with arsenazo III reagent;
- gas-volumometric determination of metallic zirconium.

For the phase composition studies the templates were prepared from rod samples for SEM/EDX analysis.

Studies of the U-Zr-O phase diagram and posttest analyses of completed tests are in progress. The combinations of components for further tests are being discussed with collaborators, a decision on compositions will be taken at the 4th CORPHAD meeting in September 2004 in Dimitrovgrad (Russia).

This section presents first preliminary results of studies on the U-Zr-O ternary phase diagram. The measured liquidus and solidus temperatures (Table 8) correspond to the Hayward phase diagram [3]. The main objective of CORD 28 liquidus temperature measurements was to check the values measured in CD 3 and CD 4. The measurements of CORD 28 and CD 3,4 coincide with the Hayward diagram [3]. The mentioned check of liquidus temperature measured CD 3 and CD 4 is explained by the minor melt pollution by carbon from graphite crucible, which may influence the liquidus temperature values. As it is evident from CORD 28 and CD 3, 4, if the difference between liquidus and solidus temperatures is insignificant, carbon has no determinable influence.

Tests CD 6 and CD 7 were performed in order to check the influence of carbon at a larger difference between liquidus and solidus temperatures. The experiments were conducted in tungsten crucibles, the startup charge had similar composition. In CD 7 the 0.32 mass.% of carbon dust was added to the melt in order to examine the influence of carbon. CD 6 had four heating and cooling cycles, at which liquidus temperature was measured. The value of liquidus temperature grew at each next cycle (the range is given in Table 8). It is necessary to note that such phenomenon had not been observed during CD 5 melting in a graphite crucible, where three heating and cooling cycles were performed. In CD 7 only one heating-cooling cycle was completed for technical reasons, and the measured liquidus temperature was by 60 °C higher than T_{liq} measured during the first cycle of CD 6. The increase of measured liquidus temperature at each next heating-cooling cycle of CD 6 can be explained by the changed radiative capacity of tungsten crucible bottom due to its gradual carbidization. The difference between liquidus temperatures measured at the initial heating-cooling cycles in CD 6 and CD 7 can be caused either by the presence of carbon dust added in CD 7 or by the technical failure, which occurred during CD 7 – it might have caused the crucible depressurization during the first heating-cooling cycle. For these reasons tests CD 6 and CD 7 have not provided a clear answer to the question about liquidus temperature sensitivity to the presence of carbon, therefore further studies are required.

Studies of the U-Zr-O ternary diagram are in progress: posttest analyses of experiments have to be completed and new measurements of other diagram sections need to be discussed, planned and implemented.

8.5 Studies of ternary oxidic systems. UO_{2+x}-ZrO_2-FeO_y

Parameters of the UO_{2+x}-ZrO_2-FeO_y eutectics point are important for thermodynamic modeling of the core melt – reactor/core catcher materials interaction. Additional studies are necessary in order to enhance the credibility and specify experimental data on this system.

Objectives of the current stage were as follows:

- to determine the composition and temperature of ternary eutectics at different oxygen potential of the system;
- to determine the final solubility of components in the formed solid solutions.

This part of experimental activities has been carried out by NITI and ISCh RAS. The oxygen potential was measured during experiments in the inert (argon) atmosphere and in air.

The preparation of eutectics composition was performed by melt crystallization in close-to-equilibrium conditions, for which the crucible containing the melt was continuously and

slowly (5÷10 mm/h) moved against inductor by the electric drive of vertical crucible shift. Under such conditions the last-to-crystallize is most fusible liquid having eutectic composition. The postphysico-chemical analysis of samples from the ingot region where last melt got crystallized, enables to determine the eutectics composition with ~ 1÷2 %mass error. The eutectics region provides samples for the DTA, VPA in the Galakhov microfurnace and SEM/EDX studies, by which the eutectics temperature is evaluated.

3 experiments have been conducted, their specification is presented in Table 9. Each experiment was preceded by thermodynamic calculations in order to forecast the ternary eutectics composition using phase diagrams of binary oxidic systems.

Table 9

Specification of tests on the UO_{2+x} -ZrO_2-FeO_y ternary eutectics studies

Test #	Initial charge, mass%					Charge mass, g
	UO_2	ZrO_2	Fe	FeO	Fe_2O_3	
Cord 25	6,8	2,9	10,	80,3	---	287,16
Cord 26	22,5	2,5	1,7	---	73,3	30,03
Cord 27	58,6	1,9	2,4	---	37,1	332,56

Cord 25 was conducted in the inert atmosphere, and Cord 26, 27 – in air.

Studies of the ternary oxidic system UO_{2+x} -ZrO_2-FeO_y are in progress. This section gives an overview of first and preliminary results of carried out studies.

Cord 25 examined the ternary eutectics point of the UO_2-ZrO_2-FeO system in the inert atmosphere.

Tests Cord 26 and Cord 27 examined the ternary eutectics point of the UO_{2+x}-ZrO_2-FeO_y system in air. Tests in air have the following peculiarity: at 1387 °C the crystallization of melt containing iron oxides features the isotherm of polymorphous transformation of magnetite into hematite. As the kinetics of complete transformation is unknown, it is necessary to perform the melt exposition below this temperature for 1÷2 hours for its saturation with oxygen from air and in order to reach its equilibrium stoichiometry. In Cord 26 the melt was exposed to 1400 °C, which did not provide conditions for magnetite – hematite transformation. Because of that Cord 27 was conducted, during which the melt was kept for 2 hours under 1350 °C, and the experimental data were used for the phase diagram construction.

The data of SEM/EDX analysis of templates produced from Cord 25 and Cord 27 ingots were used for determining the compositions of (UO_2-ZrO_2-FeO) ternary eutectics points in the inert atmosphere (Cord 25)and points of (UO_{2+x}-ZrO_2- FeO_y) in air (Cord 27). They are shown in Table 10.

Table 10

Ternary eutectics compositions of UO_{2+x}-ZrO_2-FeO_y

Test №	Eutectics composition, mass %		
	UO_2	ZrO_2	FeO
Cord 25	21,4	6,9	71,7
Test №	Eutectics composition, mass %		
	UO_{2+x}	ZrO_2	Fe_2O_3
Cord 27	62	1,8	36,2

In the inert atmosphere the measured temperature of ternary eutectics was 1321 °C.

In air (oxygen isobar - 0,21 atm.) the measured temperature of ternary eutectics was 1339 °C.

These preliminary results enable to track the position of ternary eutectics point in relation to the oxygen potential of the system.

These preliminary results on the ternary eutectics compositions and temperatures will be specified.

9. Current stage of the project implementation

The project activities of the first year have been performed in full compliance with the Work Plan, experimental matrix and its updates made after the discussion of experimental matrix and first results with collaborators. The amendments were recorded in Minutes №2 and №3 of CORPHAD-2 Steering Committee meetings, which took place on September, 2003 in St. Petersburg (Russia) and on February 9, 2004 in Paris (France). In accordance with decisions taken at the meetings the UO_{2+x} – FeO_y, UO_2 – Cr_2O_3 and (BaO, SrO)-UO_2 systems were excluded from Task 1 experimental matrix as having low and medium priority. Instead it was decided to study in more detail high-priority systems: UO_2 – FeO, ZrO_2 – FeO, SiO_2 – Fe_2O_3 (Fe_3O_4), SiO_2 – Fe_3O_4. It has been decided to keep UO_2 – SiO_2 system in the matrix, to study the available data on phase diagrams of this system and determine their credibility before taking the final decision about its presence in the project research plan. A decision on experimental series, on the UO_2-rich region in particular, will be taken at the next meeting in September 2004.

Therefore, during the 1st year of CORPHAD implementation Task 1 “Study of the binary oxidic system” has been completely fulfilled: systems UO_2 – FeO, ZrO_2 – FeO, SiO_2 – Fe_2O_3 (Fe_3O_4), SiO_2 – Fe_3O_4 have been studied completely; reports on the studies have been included into the Annual report.

Task 2 “Study of the ternary oxidic systems” including the examination of UO_2 – ZrO_2 – FeO, UO_{2+x} – ZrO_2 – FeO_y, U – Zr – O systems has been completed by 50%, which corresponds to the что the 1st year Work Plan for Task 2.

10. Cooperation with foreign collaborators

Foreign collaborators participating in the project are:

1. Dr. Karine Froment, France, CEA DTA/CEREM/DEM/SPCM, Grenoble
2. Dr. Marc Barrachin, France, IRSN/DRS/SEMAR/SEN Cadarache, Saint-Paul-lez-Durance
3. Dr. Ir. Anne De Bremaecker, France, PHEBUS SEMAR Saint-Paul-lez-Durance
4. Dr. Walter Tromm, Germany, Institut fur Kern- und Energitechnik (IKET), Karlsruhe
5. Dr. Manfred Fischer, Germany, Framatome ANP, Erlangen
6. Dr. David Bottomley, Germany, EUROPÄISCHE KOMISSION, Joint Research Centre Institut fur Transurane (ITU), Karlsruhe
7. Dr. Gerard Cognet, France, CEA/DEN/DSNI, Saclay
8. Dr. Sieghard Hellmann, Germany, Framatome ANP, Erlangen

During the 1st year the Project was implemented in close cooperation with foreign collaborators, which included the detailed discussion and updates of CORPHAD 2 Work Plan, experimental matrix, analysis and evaluation of experimental results, introduction of necessary specifications and changes into the list and inventory of planned experimental studies.

The discussion of experimental results and updates of the CORPHAD 2 experimental matrix was carried out both at joint meetings and by e-mail exchanges.

The first meeting of CORPHAD 2 Steering Committee attended by collaborators took place on April 29 – 30, 2003 in St. Petersburg (Russia). There the experimental matrix was discussed and enacted.

The second meeting of CORPHAD 2 Steering Committee was held on September 16, 2003 in St. Petersburg, Russia. The contractors presented the results of studies performed after the project start on July 1, 2003. The following presentations were made: a) Project status; b) Fragment of phase diagram ZrO_2 – FeO, c) Fragment of phase diagram UO_2 – FeO; d) First liquidus temperature measurements in the U – Zr – O system; e) Fragments of phase diagram $SiO_2 – Fe_2O_3$.

After discussion it was noted that results having practical and research value had been produced; they provide a better insight into the properties of the studied systems and have practical application in the reactor safety analysis.

Collaborators gave the following recommendations to contractors:

- to study the UO_2 – FeO и ZrO_2 – FeO systems in more detail,
- to correlate the U – Zr – O experimental studies with investigations carried out within the COLOSS project. For this the collaborators (M. Barrachin) were to give proposals for the CORPHAD-2 experimental matrix based on COLOSS project (before December 2003).
- to incorporate specific improvements and modifications into the analysis and measurement procedures.

The third meeting of CORPHAD 2 Steering Committee was held on February 9, 2004 in Paris, France. The contractors reported about the implementation of decisions made at the second meeting and presented new results produced after the second meeting. The following presentations were made:

a) Project status; b) Phase diagram of the ZrO_2 – FeO system, c) Phase diagram of the UO_2 – FeO system; d) Liquidus temperature measurements of the U – Zr – O system; e) Phase diagram of the $SiO_2 – Fe_2O_3$ (Fe_3O_4) system; e) Proposals for the experimental matrix for the period until the next meeting.

Collaborators made the following presentations:

- Preliminary measurements of the U – Zr – O melting point using the modified facility with laser heating (Dr. D. Bottomley);
- Comparison of CORPHAD, ENTHALPY and other published data with и numeric data NUCLEAR. The IRSN proposals for future tests (Dr. M. Barrachin);
- ENTALPY SYNTHESIS: Liquidus and solidus temperatures in corium-concrete mixtures (Dr. S. Hellmann).

The following decisions were taken after discussion:

- To exclude systems UO_{2+x} – FeO_y, UO_2 – Cr_2O_3 and (BaO, SrO)-UO_2 from the experimental matrix as having low and medium priority,
- The following experiments were planned for the period until the end of 2004:
  - 2 experiments with the ZrO_2 – FeO system;
  - 2 experiments with the U – Zr – O system (compositions will be discussed with M. Barrachin),
  - 1st experiment on determining the eutectics composition of the UO_2 – ZrO_2 – FeO system,
  - pretests necessary for studying the U – Fe – O system.

- A decision on the binary system UO_2 – SiO_2 will be taken at the 4th meeting of the Steering Committee, and the possibility of studying ternary systems (UO_2- ZrO_2 – SiO_2), (UO_2- ZrO_2 –CaO) in the framework of Task 2 will be decided upon later.

11. Perspectives for further investigations

The CORPHAD 2 Work Plan and experimental matrix of the 1st year, which took into account updates of the 2nd and 3rd meetings, have been fulfilled completely.

In accordance with decisions of the 3rd meeting during the first part of the 2nd year of project implementation the eutectics composition and liquidus temperature of ternary systems UO_2 – ZrO_2 – FeO и UO_{2+x} – ZrO_2 – FeO_y will be examined. Two experiments on the U – Zr – O system will be performed, the compositions of which will be discussed with Dr. M. Barrachin.

The pretests for the examination of U – Fe – O will be started, they will be performed during the 2nd year of project implementation. Decisions on the experiment to be made during the second half of the 2nd project year, including the decision about the UO_2 – SiO_2 binary system, will be taken at the 4th Steering Committee meeting on September 14, 2004 in Dimitrovgrad (Russia).

Project manager Dr. Yu. N. Aniskievich

General Director of NITI Professor V.A. Vasilenko

Appendix A

Personnel involvement during the year

Category	Man-days during the year	Incremental man-days	Total
Category I	2438	2438	6594
Category II	1404	1404	5055
Category III	140	140	360
Category IV	155.5	155.5	850

Appendix B

Main equipment procured during the 1st year

In accordance with the Work Plan the following main equipment has been procured:

1. Thermoanalyzer SETSYS Evolution (up to 2400^0C DTA, DSC) with controlled and monitored atmosphere (SETARAM, France). Cost: $135426.77.
2. Carbon express-analyzer AN-7529.1 Cost: $2 549.17.
3. Power supply unit ADC7480/12 – 3 items, total cost $7 009.49.

Project manager Dr. Yu. N. Aniskievich