ISTC1950.2-2005

Annual progress report

PROJECT № 1950.2

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

(CORPHAD 2)

(01.07.2004 – 30.06.2005)
Second year

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RUSSIAN FEDERAL AGENCY FOR ATOMIC ENERGY

July 2005

The work is financially supported by the European Union within the contract with the International Science and Technology Center (ISTC), Moscow.

Phase diagrams for multicomponent systems containing corium and products of its interaction with NPP materials (CORPHAD 2)

(1 July 2004 - 30 June 2005)

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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 at the in- and ex-vessel stages of the severe accident development with the core meltdown. The following essential characteristics have been experimentally determined: 1) concentration curves of solidus and liquidus temperatures; 2) coordinates of characteristic points: eutectics, distectics and others; 3) solubility limits of components in the solid phase; 4) temperature-concentration domains of the miscibility gap. The produced data have been used for updating the software-oriented database with previously missing or specified information on phase diagrams of oxidic and metal-oxidic systems of corium.

Experiments with oxidized and suboxidized oxidic systems were carried out on “Rasplav-2” test facility; tests with metal-oxide systems were performed on “Rasplav-3”. The method of induction melting in a cold crucible (IMCC) is used for producing corium melt. The experimental studies were partially performed in the Galakhov microfurnace and at “Tighel” installation of RSC “Kurchatov Institute”. For the experimental studies of the 2nd year the experimental facilities were modernized, the experimental methodology and methods of physicochemical analysis of uranium-bearing corium were improved.

Experiments and posttest analyses of ternary oxidic system UO_x-ZrO_2-FeO_y were performed. Melting temperature and compositions of ternary eutectics in air and inert atmosphere were evaluated; the final solubility of components in the formed solid solutions was determined. 4 experiments were conducted.

Studies of the ternary metal-oxidic system U-Zr-O have been completed. Liquidus and solidus temperatures have been determined for the sections of U-Zr-O diagram compositions recommended by collaborators; the composition of oxidic and metallic liquids coexisting in the miscibility gap has been estimated; the development of an improved methodology for evaluating the tie-line compositions in the miscibility gap has been started. 5 experiments of the CORD series have been conducted at the “Rasplav-3” tests facility and 5 experiments of the CD series at the “Tighel” facility.

Key terms: corium, phase diagram, liquidus and solidus temperature, uranium-bearing system, oxidic and metal-oxidic system, oxygen potential, severe accident at NPP.

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INTERNATIONAL SCIENCE AND TECHNOLOGY CENTER

Annual report

Project № 1950.2

1. Project title	Phase diagrams for multicomponent systems containing corium and products of its interaction with NPP materials (CORPHAD)
2. Number of annual report	2nd year report № 2-1950.2-2005
3. Main contractor	The Alexandrov Scientific Research Technological Institute (NITI) of the Russian Federal Agency for Atomic Energy, Russia 188540, Sosnovy Bor of Leningrad Oblast, NITI
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5. Date of project start	01 July, 2003
Project duration	41 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 source term reduction 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 prototypic 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 domains of the miscibility gap.

The project results will be used for:

- extension of databases with 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.

Project duration is 3 years, 5 months. During the first project year the investigation program of binary oxidic systems UO_2-FeO, ZrO_2-FeO, $Fe_2O_3(Fe_3O_4)$-SiO_2 and Fe_3O_4-SiO_2 was completed. Results of these studies were included into the Annual report for the 1st year, 5 papers prepared together with collaborators and included in the NUCLEA database.

Along with that during the first year the studies of ternary oxidic system UO_x-ZrO_2-FeO_y and ternary metal-oxidic system U-Zr-O were conducted. During the second year the studies of mentioned ternary systems were continued, as well as the studies of ternary metal-oxidic systems Zr-Fe-O and U-Fe-O. The current report present their results.

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 Kurchatov Institute (RRC KI). These installations provide conditions for studying phase diagrams under temperatures up to 2800 K and getting adequate and reliable experimental data.

The experimental complex with integrated instruments and devices 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 and programs.

The following methods are used for physicochemical analysis:

1. Analysis of elemental composition
   - 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 were refined. The experimental facility upgrading and methodology modifications are presented in Appendix 1.

8. Project implementation during the first year

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), during the 1st year experimental studies were concentrated on 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.

Phase diagram UO_2 - SiO_2 will be studied at the final stage of project implementation.

During the first year Task 2 of experimental matrix was implemented in the following way: the study of ternary oxidic system U – O – Fe was started (still in progress), and determination of UO_{2+x} - ZrO_2 - FeO_y composition and eutectic temperature was started.

The main results of complete 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 eutectic point parameters and liquidus temperature in the low-temperature domain near the eutectic point.

Therefore, the 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.

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 phase diagram study of the UO_2 – FeO system is presented in detail in the first annual report. This section gives the main results.

In experiments CORD 8, 14, 20 using BPA IMCC, VPA in the Galakhov microfurnace and DTA the eutectic point position was determined.

At this:

- The temperature of eutectics was T_{eut} = 1342 °C (in accordance with CIT Project T_{eut} = 1340 °C)
- The composition of eutectics 86.4 mass. % FeO and 13.6 mass. % UO_2 (in accordance with CIT project eutectic composition: 88.6 mass. % FeO and 11.4 mass. % UO_2)

Liquidus temperatures of the UO_2 – FeO system were determined in a wide concentration range.

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 is 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 remained unstudied.

Objectives of the completed 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 were performed. 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 metallic iron, into the melt.

The experimental study of the ZrO_2 – FeO phase diagram is presented in detail the 1st year report. This section gives the main results.

The eutectic point position was specified. Experiments CORD 2,4,5,9 gave the following results:

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

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

Liquidus temperatures of refractory compositions were determined.

Parameters of ZrO_2-based solid solutions were determined:

– cubic solid solution has the final concentration of FeO ≈ 7 mass.% at 1800 °C, the temperature range of its existence is 2700 ÷ 1800°C;

– tetragonal solid solution has the final concentration of FeO – 1,3 mass.% at 1330 °C, and the temperature range of its existence is 2347 ÷ 1172 °C.

The produced experimental data were used for the construction of the ZrO_2 – FeO phase diagram, which was identified as a simple eutectics with a domain of limited solid solutions based on several modifications of ZrO_2.

8.3 Studies of binary systems. Systems Fe_2O_3 (Fe_3O_4) – SiO_2 and 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.

Before the presented study no reliable data on Fe_2O_3(Fe_3O_4) – SiO_2 phase diagrams had been published. 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 study were as follows:

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

[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

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

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 phase diagram studies of Fe_2O_3 - SiO_2 and Fe_3O_4 - SiO_2 systems are presented in detail the 1st year report. This section gives the 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 at. respectively. The Fe_2O_3 – SiO_2 system has been found to contain magnetite (Fe_3O_4) as an additional component at 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.

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.

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.

Measurements in the Galakhov microfurnace gave liquidus and solidus temperatures of the Fe_3O_4 - SiO_2 system.

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 of the Fist-year report. 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.

9. Experimental studies during the reported year and main results

In accordance with the CORPHAD 2 Work Plan and its updates registered in Minutes № 2, № 3 and № 4 of the project Steering Committee, which took place on 17 September 2003in St. Petersburg, Russia, 9 February 2004 in Paris (France) and 14 September 2004 in Dimitrovgrad, Russia, during the 2nd year of project implementation the study of ternary oxidic system as specified by the project objectives; ternary metal-oxidic systems U-Zr-O, U-Fe-O, Zr-Fe-O were studied in the scope and for compositions listed in Minutes № 3 and № 4. Following the proposal of S. Hellmann two tests with ternary system UO_2-ZrO_2-FeO (instead of originally planned one) were performed in order to specify eutectics temperature and composition (Minutes № 4). For the U-Zr-O system it was decided to make one of the tests with the following composition: UO_2 60 mol % - Zr 40 mol %. For this laser methodology of the ITU was applied; its results were reported by M. Sheindlin. For the U-Fe-O system a test with composition mol %: U – 60 %, Fe – 20 % (Minutes № 4) was planned. In accordance with recommendation of Dr. Hellmann experiments on the oxidation kinetics were excluded from the Work Plan (Task 4), they were replaced by a higher priority tests (Minutes № 4).

The results of studies completed during the 2nd year are presented below.

9.1. Ternary oxidic systems. System UO_x-ZrO_2-FeO_y

The UO_x-ZrO_2-FeO_y system is the basic one used for describing phenomena taking place at a severe accident at the VVER, PWR, BWR reactors. In order to model phenomena accompanying corium interaction with materials containing iron, zirconium and their oxides, also processes of resulting melt crystallization, it is important to know parameters of ternary eutectic points (temperature and composition) and final solubility of components in each other, if the system contains solid solutions.

Two following domains of the diagram are important for of reactor conditions:

- having low oxygen potential typical for the in-vessel stage of severe accident (early stage) in presence of metallic zirconium;
- corresponding to fully-oxidized corium during the ex-vessel or late stage of the in-vessel accident.

There is a limited inventory of published data in a narrow concentration range on phase equilibria in the considered ternary oxidic systems. At the same time models based on available binary diagrams UO_2-FeO, ZrO_2-FeO and UO_{2+x}-FeO_y, ZrO_2-FeO_y corresponding to a low oxygen potential and air - on one hand and data of experiments in air – on the other - gave different concentration domains of the ternary eutectic point. For this reason the specified experimental data on the temperature and composition of the ternary eutectic point at low oxygen potential in the system and in the oxidizing atmosphere are necessary for updating the NUCLEA database and verification of the thermodynamic code GEMINI.

The work objectives were:

- determine melting temperature and composition of ternary eutectics in air and inert atmosphere;
- determine final solubility of components in the formed solid solutions.

Experiments were conducted on the "Rasplav 3" tests facility. Liquidus temperature was measured during the local cooling of the melt surface by changing the position of water-cooled electromagnetic screen along the axis.

The ingot having an eutectic composition was formed by melt crystallization in the close-to-equilibrium conditions, by slow (5÷10 mm/h) continuous movement of crucible with melt versus the inductor. In these conditions the most fusible liquid, i.e. liquid having the eutectic composition, is the last to crystallize The physicochemical analysis of samples from this zone gives an approximate composition of eutectics. To specify the eutectic point the test was repeated, for the second test the composition of initial charge corresponded to the approximate eutectic composition identified in the first test, the experimental procedure was repeated. An error of determining eutectic composition using this method is ≈1÷2 mass %.

The pretest calculations of the experimental results were performed using the available data on components of the binary system, eutectic points of which had been determined experimentally in the inert atmosphere during the first year of the CORPHAD 2 project; for air data were taken from publications.

Composition and temperature of the ternary eutectics were studied by the DTA, VPA in the Galakhov microfurnace and SEM/EDX analysis.

Four experiments have been conducted: CORD 25, CORD 26, CORD 27 and CORD 31. Detailed results of the studies are given in Appendix 1. Main results of experiments and physicochemical analysis are summarized below.

The initial charge compositions are given in Table 1.

Table 1. Initial components of tests CORD 25, 26, 27, 31

CORD	**Content, mass % / mol %**							**Charge mass, g**	**Atmosphere**
	UO_2	$UO_{2,24}$	ZrO_2	Fe	Getter (Fe)	FeO	Fe_2O_3		
25	6,8/1,9	-	2,9/1,8	9,0/ 11,9	1,0/1,3	80,3/ 83,1	-	287,2	Ar
26	22,5/ 14,1	-	2,5/3,4	1,7/5,0	-	-	73,3/ 77,4	300,0	Air
27[1)]	-	58,6/ 42,3	1,9/3,1	2,4/8,6	-	-	37,1/ 45,9	332,6	Air
31[2)]	21,1/ 6,7	-	6,8/4,7	6,6/ 10,1	1,0/1,5	64,5/ 77,0	-	304,7	Ar

[1)] initial charge composition for this experiment was determined from results of CORD 26 (in air)

[2)] initial charge composition for this experiment was determined from results of CORD 25 (in the inert atmosphere)

The specific feature of experiments in air is that during the crystallization of melt containing iron oxides, an additional process of Fe_3O_4 interaction with oxygen produces Fe_2O_3. Temperature of Fe_3O_4 oxidation to Fe_2O_3 is 1387ºC, but as the process kinetics is not known, the experimental procedure in air included the melt exposition during 1-2 hours below this temperature in order to establish chemical equilibrium.

Experiments CORD 25 and CORD 31 were conducted in the inert atmosphere, and CORD 26 and CORD 27 in air. In CORD 26 due to the charge composition, different from the eutectic one, the long-term melt exposition at temperature below 1387ºC was not achieved (it was 1400ºC), and this did not guarantee the establishment of chemical equilibrium at Fe_3O_4 oxidation to Fe_2O_3, therefore it could result in erroneous data on eutectic composition and temperature. To ensure conditions for the melt enriched with oxygen in CORD 27 the initial charge composition was changed, and exposition at 1350÷1370ºC was performed. To confirm the oxidation degree of U and Fe the thermogravimetry (TGA) analysis of a sample from the eutectic part of the CORD 27 ingot was made. Results of chemical analysis before and after TGA prove the equilibrium of coexisting phases.

The following data were provided by experiments and physicochemical analyses:

1. Experiments in the inert atmosphere (CORD 25, CORD 31) produced data on the ternary eutectics composition and temperature in the UO_2-ZrO_2-FeO system, which are
   - composition mol %: UO_2 – 3,6; ZrO_2 – 4,9; FeO – 91,5;

     (mass %: UO_2 – 11,8; ZrO_2 – 7,4; FeO – 80,8)
   - temperature: T_{eut}=1318±5ºC.

   The temperature of ternary eutectics is lower than that of binary eutectics in the UO_2-FeO and ZrO_2-FeO systems, which confirms the credibility of results.
2. In the UO_2- ZrO_2-FeO system the final solubility of FeO in the UO_2 (ZrO_2, FeO)-based solid solution, which was 8±2 mol % (2,5±1 mass %) FeO. It should be noted that due to the crystallization peculiarities of this system the FeO solubility limit in the UO_2-based solid solution can be lower than actual due to its decomposition into U (Zr) O_2 and FeO.
3. Experiment in air (CORD 31) determined the composition and temperature of ternary eutectics in the U_3O_7-U_3O_8-ZrO_2-FeO_2-$FeO_{1,5}$ system, which are:
   - composition mol %: UO_{2+x} – 32 %; ZrO_2 – 2,1 %; Fe_2O_3 – 65,9 %;

     (mass %: UO_{2+x} – 61,04 %; ZrO_2 – 1,74 %; Fe_2O_3 – 37,22 %)
   - temperature: T_{eut}=1339±5ºC.

   The temperature of ternary eutectics is lower than temperature of binary eutectics in the UO_{2+x} – FeO_y and ZrO_2 – FeO_y, systems known from publications.
4. In the U_3O_7-U_3O_8-ZrO_2-FeO_2-$FeO_{1,5}$ system the final solubility of FeO_y in the UO_{2+x} (ZrO_2, FeO_y) solid solution was evaluated, it was approx. 3,2±0,8 mol.% $FeO_{1,5}$ (1,9±0,5 mass % Fe_2O_3).

9.2. Ternary metal-oxidic systems. System U-Zr-O

Phase diagram of the ternary metal-oxidic system U-Zr-O is important for modeling one of the essential processes of the core degradation at a severe accident – interaction of oxidic uranium with zirconium in the conditions of oxygen deficit. But until present difficulties accompanying the experimental studies of this system prevented the acquisition of all data for different sections of the ternary diagram depending on the oxygen concentration. These difficulties are explained by a) extremely high chemical activity of melts in the concentration domain of interest, which makes the cold crucible technology most suitable for these studies, b) easy stratification of this system.

These studies had the following objectives :

- Study liquidus and solidus temperatures for the compositions of the U-Zr-O ternary diagram sections, which were recommended by collaborators.
- Determine compositions of coexisting oxidic and metallic liquids in the miscibility gap.

- Develop adequate methods and experimental facilities for determining liquidus and solidus temperatures, the miscibility gap composition and tie-lines.

The properties of the studied metal-oxidic system restrict the application of traditional thermal analysis methods for the whole range of compositions, especially in the high-temperature region. For this reason NITI and ISHc RAS developed new methodologies for determining T_{liq} and T_{sol} , and built experimental setups to apply them.

In accordance with updated Work Plan for the 2nd Phase of the project and using compositions recommended by collaborators 10 experiments were conducted: 5 of the CORD series and 5 of the CD series. Tables 2 and 3 present their experimental matrixes.

Table 2. CORD experimental matrix

Experiment	Charge composition, at. %			Mass,	Objective
	U	Zr	O	г	
CORD-28-I	8	52	40	300,0	Measure T_{liq}, T_{sol}
CORD-28-II	13	43	44	423,9	Measure T_{liq}, T_{sol}
CORD-29	20	17	63	400,0	Measure T_{liq}
CORD-34	22	33	45	446,1	Measure T_{liq}, T_{sol}
CORD-37	33	27	40	505,2	Measure T_{liq}, tie-line

Table 3. CD experimental matrix

Experiment	Charge composition, at. %			U/Zr	Objective
	U	Zr	O		
CD-1	22,9	19,1	58,0	1,2	Measure T_{liq}
CD-2	25,7	15,8	58,5	1,63	Measure T_{liq}
CD-3	13,0	43,0	44,0	0,3	Measure T_{liq}, T_{sol}
CD-4	8,0	52,0	40,0	0,15	Measure T_{liq}, T_{sol}
CD-5	16,0	36,0	48,0	0,44	Measure T_{liq}, T_{sol}

“Rasplav-3” experimental setup was developed for the CORD series; the original methodology of VPA IMCC previously tested in the studies of binary oxidic systems was further improved and used for determining T_{liq}.

The methodology for determining T_{liq} of metal-oxidic system included the following stages:

- molten pool was formed on a thin water-cooled bottom;
- melt was superheated to $T_p > T_{liq}$;
- molten pool depth and bottom crust thickness were measured;
- surface of the superheated pool was cooled by moving it against the inductor (or by moving electromagnetic screen in case of CORD 28-I and 28-II); surface temperature was registered until the solid phase was formed;
- melt superheating and cooling was repeated several times;

- melt surface temperature was measured and registered using the video recording system combined with the spectral ratio pyrometer RAYTEK MR-1-SC;
- posttest frame-by-frame analysis of the recorded thermogram was made and minimum temperature of the melt (T_{liq}) was determined;
- posttest physicochemical analysis of samples was made, their properties determined.

T_{sol} in the CORD series was determined by the VPA in Galakhov microfurnace. It was not possible to measure T_{liq} by this method, because samples interacted with holder manufactured from molybdenum, tungsten or iridium at temperatures representing T_{liq} of metal-oxidic samples. For some sample compositions having a high T_{sol}, the T_{sol} measurement was not authentic, considerably lower than actual, because the interaction of sample and holder took place.

The CD series aimed at measuring liquidus and solidus temperatures was performed in ac cold crucible of the “Tigel” experimental facility of the RSC “Kurchatov Institute”. Thermal phenomena were determined using the method of thermogram differentiation.

The methodology for determining T_{liq} and T_{sol} of specified compositions in the CD series was as follows:

- molten pool in the crucible was produced, superheated and homogenized;
- after the pool homogenization the heating was disconnected, and temperature of the cooled melt was measured with pyrometer;
- posttest analysis of the thermogram using the differentiation method enabled to identify thermal phenomena taking place at T_{liq} and T_{sol}.

Crucibles for the CD series were manufactured from the gas-phase tungsten (CD 1 and 2) and graphite coated with zirconium carbide (CD 3-5). Crucible had a cover made from tungsten, tantalum or graphite. The graphite ohmic heater was used.

Main problem, to be resolved during the preparation of these experiments was the crucible material – its possible interaction with metal-oxidic melt had to be prevented. Gas-phase tungsten showed good resistance to corium with a high oxygen content (> 58 at.%). For coria with a low oxygen content a good solution was the graphite crucible having zirconium carbide coating.

Table 3 shows that experiments of CD series used compositions found near the section of quasibinary diagram of UO_2-$ZrO_{0,43}$. To prove that T_{liq} measured in the CD experiments was not influenced by the presence of crucible materials CORD tests (28-1 and 28-2), were performed, in which CD compositions (CD 3 and 4) were reproduced. Both groups of experiments had close results both in terms of sample composition and liquidus temperature.

CORD compositions have a wider concentration range and are located close to the miscibility gap in order to determine the gap boundaries. Melt composition in CORD 29 is close to the UO_2-ZrO_2 section. CORD 34 was aimed at comparison its results with experimental data produced within COLOSS program in the ITU (Karlsruhe, Germany), where the laser technique was applied for measuring T_{liq} and T_{sol}. Melt composition is close to the UO_2-Zr section. The predetermined melt composition in CORD 37 was surely within the miscibility gap, so the experiment was aimed at refining the tie-line construction methodology.

To guarantee the reliability of measured values and increase data inventory the posttest analysis of samples from these series was performed using the following methods, which complement and sometimes duplicate each other:

- Chemical analysis.
- X-ray fluorescence (XRF) using spectrometer SPECTROSCAN MAX-GV for the elemental analysis of molten products.

- SEM/EDX methods for determining the microstructure and elemental composition of the samples. For SEM analysis the scanning electron microscope CamScan MV2300 was used, EDX analysis was made using micro-probe device Oxford Link Pentaflet. SEM method was adapted to oxygen measurement (SEM/density).

The studies of metal-oxidic system U-Zr-O provided the following results:

1. One of the main objectives of the U-Zr-O studies was to determine liquidus and solidus temperatures of compositions recommended by collaborators.

- Table 4 gives T_{liq} measured by VPA IMCC and T_{sol} measured by VPA in Galakhov microfurnace in the CORD series.

Table 4. Temperatures measured by VPA IMCC and VPA in Galakhov microfurnace, respectively

Test	Calculated melt composition: charge + spillages, at. %			Composition of melt samples, XRF, at. %			T_{liq}, ºC	T_{sol} [3], ºC
	U	Zr	O	U	Zr	O		
CORD-28-I [1]	7,7	53,6	38,7	7,7	53,7	38,6	2085	-
CORD-28-II [1]	13,0	43,9	43,2	12,9	43,9	43,2	2170	1976
CORD-29 [1]	20,0	17,1	63,0	19,8	17,2	63,0	2461	-
CORD-34 [1]	22,1	33,8	44,1	21,5	34,7	43,8	2302 2307 2305	2150
CORD-37 [2]	32,5	28,2	39,3	21,7	27,7	50,5	2326 2330	1842

Note 1. In CORD experiments (28-I, 28-II, 29, 34) melt composition is different from that of the charge due to the incomplete charge melting and presence of crust, which is usually enriched with a refractory phase (uranium oxide).

Note 2. Charge of CORD 37 ensured the melt presence inside the miscibility gap. In the close to quenching conditions of melt cooling the top and bottom ingot parts were formed, which had compositions close to the stratified liquids. Top oxidic part of the ingot had a homogeneous dendrite structure similar to the CORD-34 ingot. The bottom metallic part consisted of the matrix of (UZr)O solid solution with dendrite inclusions αZr(O), the structure and composition of this half-ingot had a vertical inhomogeneity. At 2328ºC compositions of the top (oxidic) and bottom (metallic) liquids are as follows:

- top (oxidized), at.%: U-21,7; Zr-27,7; O-50,5
- bottom (metallized), at.%: U-33,5; Zr-42,7; O-23,7.

In Table 4 CORD 37 charge composition corresponds to liquidus temperature (monotectics), and composition of the top liquid – to solidus temperature

Note 3. In CORD-28-I and CORD-29 it was not possible to determine T_{sol} by the VPA in Galakhov microfurnace (Table 4) due to the interaction of holder and sample. This can influence measured T_{sol} values in other CORD experiments, if T_{sol} is high enough, it results in the measured T_{sol}, which is lower than actual.

- T_{liq} and T_{sol} measured by the thermogram differentiation method in the CD series are given in Table 5.

Table 5. T_{liq} and T_{sol} measured in CD series

Test	Melt composition, charge1), at. %			T_{liq}, ºC	T_{sol}, ºC
	U	Zr	O		
CD-1	22,9	19,1	58,0	2370	-
CD-2	25,7	15,8	58,5	2400	-
CD-3	13,0	43,0	44,0	2135	2072
CD-4	8,0	52,0	40,0	2100	2085
CD-5	16,0	36,0	48,0	2225	2025

Note 1. Melt composition in the CD series was determined from the charge, because the hot crucible provides complete melting of charged materials, no losses. Insignificant melt pollution with carbon detected in the analysis does not produce a significant influence on the average composition.

Note 2. Comparison of T_{liq} and T_{sol} for practically identical compositions in experiments CORD 28 (I and II) and CD 3, 4 (tables 4 and 5) shows their similar values, which testifies to the negligible influence of small carbon concentrations on T_{liq} and T_{sol} in the CD experiments.

2. Measured liquidus and solidus values were compared to thermodynamic calculations in the program GEMINI-2 / NUCLEA-05. Table 6 gives the comparison results.

Table 6. Measured and calculated T_{liq} and T_{sol} for compositions of experimental series CORD, CD and an ITU experiment from EC COLOSS project

Experiment	**Composition , at.%**			**Experiment**		**Calculation**		**Note**
	U	Zr	O	T_{liq}, K	T_{sol}, K	T_{liq}, K	T_{sol}, K	
CORD-28-I	7,7	53,7	38,6	2358	-	2238	2076	T_{sol} measurement was not possible
CD-4	8,0	52,0	40,0	2373	2358	2231	2092	
CORD-28-II	12,9	43,9	43,2	2443	2249	2357	1917	
CD-3	13,0	43,0	44,0	2408	2345	2362	1985	
CD-5	16,0	36,0	48,0	2498	2298	2426	1988	
CORD-29	19,8	17,2	63,0	2734	-	2803	2103	T_{sol} measurement was not possible
CORD-34	21,5	34,7	43,8	2578	2423	2470	1703	• Stratification not determined experimentally • Stratification predicted by calculations
COLOSS (ITU test)	22,0	33,0	44,0	2550	2550	2486	1703	• Stratification not determined experimentally • Stratification predicted by calculations
CORD-37	21,7	27,7	50,5	2601	2115	2522	1690	• Oxidic liquid composition is given • Stratification not determined experimentally • Stratification predicted by calculations

The following conclusions can be made using the data of Table 6:

- Difference between measured and calculated liquidus temperature values do not exceed ~ 100 K, which confirms the acceptable accuracy of numerical thermodynamic modeling.
- Difference between experimentally measured and calculated values of solidus temperature is ~ 700 K. Taking into account that T_{sol} measured by VPA in Galakhov microfurnace can be lower than actual due to the interaction with holder material, the difference between measured and calculated temperatures may be even larger. This testifies to the inadequate accuracy of T_{sol} thermodynamic modeling by the GEMINI-2 program. We should note that CORD and CD solidus temperature differs considerably not only from the calculated values, but also from the numerous experimental results of Oleander, Hoffman and Hyward on zirconium dissolution in uranium oxide produced during the studies of pseudobinary diagrams U-Zr-O. In these experiments solidus temperature was equal to the temperature of eutectics and was much lower than solidus temperature measured in CORD and CD series. But this is just an apparent controversy. Indeed, the published data report the studies of the ternary diagram domain, where the liquid has a eutectic composition. In the eutectic systems with complete insolubility of components solidus surface crosses the eutectic point, and it is parallel to the diagram baseline. In CORD and CD experiments the U-Zr-O system was studied in the solid solution domain, for which the solidus surface includes both horizontal and upward surfaces of limited solid solutions, in which solidus temperature can be substantially higher than eutectics.
- In CORD-34 the stratification of liquids was not observed, though the numeric model predicted it, and in CORD-37 the tie-line ends are within the miscibility gap boundary predicted by the GEMINI calculations. This enables to assume that the miscibility gap in the system has a smaller concentration interval in comparison to the calculated data.
- In CORD-34 for the cross-verification of experimental results and comparison with GEMINI-2 thermodynamic calculations the prepared melt composition was similar to ITU-EC COLOSS composition studied using the laser pulse heating method. It can be seen from Table 6 that liquidus temperatures measured by different methods for the same composition are in a good agreement with each other and calculations.

3. The main difficulty encountered at determining compositions of metal-oxidic systems, especially in the miscibility gap, is in the quantitative evaluation of oxygen content. Different methods and assumptions are used for the approximate evaluation of its content.

The methods and their limitations are presented below:

- SEM/EDX analysis combined with microprobe measurements of oxygen and calibration using reference substances enables to get reliable data on the cation composition and oxygen content in separate phases. A limitation of this method is in the difficulty of correlating the average composition of microsections evaluated by scanning with the total average composition due to the small area of scanning and inhomogeneity of compositions. A very big number of measurements have to be made for getting acceptable accuracy.
- XRF also enables to determine the cation composition of samples. Using this method oxygen is calculated from the residue; and the measurement results are sensitive to oxygen concentration due to the matrix effect.
- Chemical analysis enables to determine U and Zr concentrations in the sample. Oxygen can be evaluated only from the residue.
- SEM/density methodology was developed for the oxygen evaluation during the project implementation. It determines oxygen content using: the SEM analysis data of volumetric fraction of coexisting phases; assumption that oxygen dissolution data of previously

determined compositions are close at similar stoichiometry; determined density of solid solution assuming the additivity of its components' densities, close compositions of melt and charge. The mentioned assumptions and factors are used for thermodynamic and geometrical plotting in the U-O-Zr triangle. As information about phase equilibria in the miscibility gap are important and experimental data are limited this methodology will be refined during further studies outside CORPHAD 2 framework.

- At present alternative methods of oxygen measurement are developed – carbometric reduction of samples containing oxygen, and gas-volumetric method. But the adaptation of these methods will require a large volume of targeted time- and labor-intensive studies. Therefore it cannot be completed within the current CORPHAD project.

10. Current stage of project implementation

Work within the project carried out during the 2nd year was in full compliance with the Work Plan, experimental matrix and its updates made after the discussions of produced results with collaborators, the decision were recorded in the minutes №2, №3 and №4 of the CORPHAD 2 Steering Committee meetings, which were organized on 17 September 2003 in St. Petersburg, Russia; 9 February 2004 in Paris, France and 14 September 2004 in Dimitrovgrad, Russia. In accordance with conclusions about the matrix and Work Plan for the period of project prolongation without additional budget it was decided:

- Task 1: exclude UO_{2+x} – FeO_y, UO_2 – Cr_2O_3 and (BaO, SrO)-UO_2 system from the experimental matrix as having average and low priority. Study the UO_2 – SiO_2 system (2 point for compositions having average concentrations) during the CORPHAD prolongation without additional budget.
- Task 2: exclude UO_2 – ZrO_2 – SiO_2 and UO_2 – ZrO_2 – CaO systems from the experimental matrix. Include these systems into the proposal for a new ISTC project CORPHAD-P.
- Task 3: corium oxidation kinetics to be excluded from the experimental matrix.
- Instead of tests excluded from the experimental matrix perform an in-depth and detailed analysis of high-priority systems, primarily metal-oxidic systems in the miscibility gap.

During the 2nd year of CORPHAD implementation the study of eutectic composition and temperature of the ternary oxidic system UO_x – ZrO_2 – FeO_y was completed and final solubility of components in each other was determined. Report on Task № 2 has been made.

The phase diagram study of metal-oxidic system U-Zr-O has been completed (10 points: CORD-28(I, II), CORD-29, CORD-34, CORD-37, CD-1, CD-2, CD-3, CD-4, CD-5). Studies of metal-oxidic systems U-Fe-O, Zr-Fe-O have been studied. Studies of these systems will be continued.

During the 2nd year Task 2 was completed by 75 %, which is in full compliance with updated Work Plan.

11. 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, AREVA NP GmbH, Erlangen.
6. Dr. David Bottomley, Germany, EUROPAISCHE KOMISSION, Joint Research Center Institut fur Transurane (ITU), Karlsruhe.
7. Dr. Gerard Cognet, France, CEA/DEN/DSNI, Saclay.
8. Dr. Sieghard Hellmann, Germany, AREVA NP GmbH, Erlangen.
9. Dr Pascal. Piluso, France, CEA/DEN/DSNI, Cadarache.
10. Dr. Florian Fichot). France, IRSN/DRS/SEMAR/CEN, Cadarache.
11. Professor Frank-Peter Weiss, Germany, Forschungszentrum Rossendorf, Drezden.

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 completed experiments, discussion of compositions for each planned experiment, determination of its specifications and posttest physicochemical analysis. The experimental program was accompanied by the numeric modeling of test results using the thermodynamic code GEMINI; comparative analysis of data produced within projects ENTHALPY, CIT, COLOSS; preparation of joint publications on the results of completed tests.

This interaction during the 2nd year of project implementation was performed during meetings (№ 4 and № 5) of the Project Steering Committee and by continuous information exchange by e-mail. The project was also discussed at meetings № 6 and № 7 of CEG-SAM.

The 4th meeting of CORPHAD 2 Steering Committee took place on 14 September 2004 in Dimitrovgrad, Russia. The contractors made the following presentations: a) Project status; b) Phase diagram of the UO_2 – FeO system; c) Phase diagram of the ZrO_2 – FeO system; d) First results on the studied phase diagrams of U – Zr – O, Fe – Zr – O and UO_2 – ZrO_2 – FeO_y.

Collaborators made the following presentation: Sheindlin M., Further melting point determinations of the U – Zr – O system.

The 5th meeting of the CORPHAD 2 Steering Committee took place on 13 July 2005 in St. Petersburg, Russia. The contractors made the following presentations: a) Project status; b) CORPHAD progress, c) proposals for the project prolongation with additional budgeting.

Collaborators prepared the following presentations:

a) S. Hellmann, Relevance of CORPHAD investigations for severe accident topics; б) M. Barrachin, Application of CORPHAD results to NUCLEA database development: current status and future needs.

Jointly with collaborators a justification for project prolongation for 5 months without additional budget was prepared; 5 papers were prepared.

12. Perspectives for further investigations

The updated Work Plan and Experimental matrix for the CORPHAD-2 2nd year have been completed.

In accordance with decisions of the Steering Committee (Minutes № 3, № 4, № 5) during the 3rd year of project implementation 5 experiments will be performed on the following systems: 1) U-Fe-O (2 experiments); 2) U-Zr-O (1 experiment in the miscibility gap); 3) U-Zr-Fe-O (2 experiments); 4) multi-component prototypic system (1 experiment). During the 5 months of added project time (without additional budget) 2 tests with the SiO_2 – UO_2 system will be performed.

Compositions for the studied systems will be determined and discussed with collaborators.

Project manager	Dr. Yu. N. Aniskevich
General Director of NITI	Professor V.A. Vasilenko

Appendix A

Personnel involvement during the 2nd year

Category	Man-days during the year	Incremental man-days	Total
Category I	2514.5	4952.5	6594
Category II	2314	3718	5055
Category III	205	345	360
Category IV	62	217.5	850

Appendix B

Main equipment procured during the 2nd year

In accordance with the Work Plan the main equipment has not been procured during the 2nd year.

Project manager Dr. Yu. N. Aniskevich

ATTACHMENT 1

ABSTRACTS OF PAPERS, PRESENTAIONS AND REPORTS PREPARED DURING 2ND YEAR OF THE PROJECT IMPLEMENTATION

1. Abstract of paper in the Journal of Nuclear Materials, in press

Phase diagram of the ZrO_2-FeO system

S.V. Bechta[a], E.V. Krushinov[a], V.I. Almjashev[b], S.A. Vitol[a], L.P. Mezentseva[b], Yu.B. Petrov[c], D.B. Lopukh[c], V.B. Khabensky[a], M. Barrachin[d], S. Hellmann[e], K. Froment[f], M.Fischer[e], W. Tromm[g], D. Bottomley[h], F. Defoort[f], V.V. Gusarov[b]

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[g] FZK, IKET, Karlsruhe, Forschungszentrum Karlsruhe GmbH, P.O. Box 3640, D-76021 Karlsruhe, Germany

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The results on the ZrO_2-FeO system studies in a neutral atmosphere are presented. The refined eutectic points have been found to correspond to a ZrO_2 concentration of 10.3±0.6 mol% at 1332±5ºC. The final solubility of iron oxide in zirconia is determined in a wide temperature range, taking into account the ZrO_2 polymorphism. A phase diagram of the pseudobinary system in question has been constructed.

2. Abstract of paper in Journal of Inorganic Chemistry (in print)

Phase ratios in the ZrO_2-FeO system

S.V. Bechta*, E.V. Krushinov*, V.I. Almjashev**, S.A. Vito*, L.P. Mezentseva**, Yu.B. Petrov***, D.B. Lopukh***, V.B. Khabensky*, M. Barrachin****, S. Hellmann*****, V.V. Gusarov**

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**** Institut de Radioprotection et Surete Nucleaire (IRSN), Paris, France

***** Framatome ANP GmbH, Erlangen, Germany

Quasi-binary phase diagram of the ZrO_2-FeO system in the inert atmosphere (Ar) is constructed. It is a diagram with eutectics and region of FeO limited solid solutions in ZrO_2. Eutectic composition and temperature in the system have been specified as corresponding to ZrO_2 content of 10.3±0.6 mol. % and 1332±5ºC.

Parameters of FeO final solid solutions in ZrO_2 are determined: *c*- ZrO_2(FeO) exists in the temperature range 2710-1800ºC, maximum value of the final solubility of FeO in ZrO_2 at ~1800ºC corresponds to ~13 mol. % FeO; *t*-ZrO_2(FeO) exists in the temperature interval 2347-1172ºC, maximum value of the final solubility of FeO in ZrO_2 – 2.2±0.3 mol. % at 1332ºC.

3. Abstract of paper in the Journal of Radiochemistry (in print)

Phase transformations in the binary cross-section of the UO_2-FeO-Fe system

S.V. Bechta[1], E.V. Krushinov[1], V.I. Almjashev[2], S.A. Vitol[1], L.P. Mezentseva[2], Yu.B. Petrov[3],
D.B. Lopukh[3], N.A. Lomanova[2], V.B. Khabensky[1], M. Barrachin[4], S. Hellmann[5], K. Froment[6], M. Fisher[5],
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Phase transformations in the oxidic binary cross-section of the UO_2-FeO-Fe system have been studied. Temperature, at which components of the heterogeneous UO_2-FeO system start to melt, is evaluated as 1335±5°C; and the fusibility curve of the system is constructed. Final solubility of FeO in the urania-based solid solution is determined as ~ 17 mol % FeO. Structural changes of crystals at the formation of solid solution are determined. Absence of UO_2 solubility in the Wustite-based phase (FeO) is proved.

4. Abstract of paper in the Journal of Inorganic Chemistry (in print)

Phase and chemical transformations in the SiO_2-Fe_2O_3(Fe_3O_4) system at different partial pressures of oxygen

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The SiO_2-Fe_2O_3(Fe_3O_4) system is studied in air, oxygen and inert atmosphere. Iron oxide dissociation temperatures, melting start temperatures, complete melting of coexisting phases and melt stratification depending on the oxygen partial pressure are determined. The scheme of phase and chemical transformations in the considered systems is presented.

5. Abstract of paper in the Journal of Nuclear Materials (in print)

Phase diagram of the UO_2-FeO_{1+x} system

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Phase-relation studies of the UO_2-FeO_{1+x} system in the an inert atmosphere are presented. The eutectic point has been determined, which corresponds to a temperature of (1335±5)ºC and a UO_2 concentration of (4.0±0.1) mol.%. The maximum solubility of FeO in UO_2 at the eutectic temperature is estimated as (17.0±1.0) mol.%. Liquidus temperatures for a wide concentration range are determined and a phase diagram of the system has been constructed.

6. **Abstract of presentation at the Conference The first European Review Meeting on Severe Accident Research (ERMSAR-2005),** Aix-en-Provence, France, 14-16 November 2005

CORPHAD and METCOR ISTC projects

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The ongoing CORPHAD Project (Phase Diagrams for Multicomponent Systems Containing Corium and Products of its Interaction with NPP Materials) was started in August 2003. The main aim of the project is to experimentally determine the relevant experimental data on phase diagrams of binary, ternary, quaternary and prototypic multi-component systems, which are important for analysis and modeling of a severe accident (SA) and efficient planning of severe accident management (SAM) measures. The data should be directly used for the European NUCLEA database development and validation. The following systems are in the focus of the project: (1) UO_2 - FeO, (2) ZrO_2 – FeO, (3) SiO_2 – Fe_2O_3, (4) UO_2 - SiO_2, (5) UO_2 - ZrO_2 – FeO, (6) UO_2 - ZrO_2 – FeO_y, (7) U-O-Fe, (8) Zr-O-Fe, (9) U-O-Zr, (10) U-Zr-Fe-O, (11) complex corium mixtures.

The experimentally determined data of the listed diagrams include: coordinates of characteristic points (eutectics, peritectics and others); liquidus and solidus concentration curve; component solubility limits in the solid phase; tie line coordinates and temperature-concentration regions of the miscibility gap. Different methodologies are used for the diagram study. Classical methods of thermal analysis, like DTA and DSC are combined with methods specifically developed for corium studies.