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The UO_2–ZrO_2 system at high temperature ($T > 2000$ K): importance of the meta-stable phases under severe accident conditions

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Abstract

In the framework of the severe accident R&D studies led by CEA, a better knowledge of 'corium', mainly a UO_2–ZrO_2 mixture, which would result from the melting of a nuclear reactor core, is fundamental to mastering this kind of hypothetical accident. Among the available corium physical characteristics, the knowledge of the final crystalline compounds and their quantities gives basic information about the physico-chemistry mechanisms and the solidification path (thermodynamic calculation). Meta-stable phases in the UO_2–ZrO_2 system (tetragonal solid solution), which appear during transient phases of severe accidents, have been observed in a recent real material experiment. A specific XRD (X-ray diffraction) approach has been developed for corium analysis coupling identification of the solid solutions and Rietveld method for quantitative data. Similar transient phases had been characterized on samples coming from TMI-2 nuclear reactor corium samples.

1. Introduction

In the hypothetical case of a nuclear reactor severe accident, the reactor core could melt and form a mixture, called 'corium', of highly refractory oxides (UO_2, ZrO_2) and metallic or oxidised steel, that could eventually flow out of the vessel and mix with the substrate decomposition products (generally oxides such as SiO_2, Al_2O_3, CaO, Fe_2O_3). The French Atomic Energy Commission (CEA) has launched an R&D programme aimed at providing the tools for improving the mastering of severe accidents. The improved knowledge of the corium behaviour (mainly a UO_2–ZrO_2 mixture), which could form from the melting of a nuclear reactor, is crucial to mastering this kind of severe accident [1,2].

In order to interpret a severe accident scenario or an experiment, one important point concerns the determination at a given temperature of the existing phases, and their proportions. This can be made in a first step assuming a thermodynamic equilibrium, with a phase diagram for simple mixtures, like (pseudo-) binary or (pseudo-) ternary mixtures, or using a thermodynamic code (Gibbs energy minimizer [3]) and database (e.g. the TDBCR or NUCLEA databases [4]). Such a work has been done in the framework of the European ENTHALPY project [5].

But, during the different stages of severe accidents, some transient phases can occur. In those cases, the thermodynamic equilibrium cannot be reached. Some recent

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experiments of corium melting/spreading on the PLINIUS platform at CEA-Cadarache have shown the existence of meta-stable phases in the UO_2–ZrO_2 system.

The paper describes an UO_2–ZrO_2 corium melting and spreading experiment (VULCANO VE-U8) [6], and the post-test analysis, especially the X-ray diffraction which is the reference method used to characterize the corium phases coming from the different PLINIUS facilities, and the thermodynamic approach. A specific method for identifying $U_{1-x}Zr_xO_2$ solid solutions has been developed, and the validity of quantitative analysis of corium crystalline phases using the Rietveld method has been tested. Evidence of the existence of a meta-stable ($U_{1-x}Zr_xO_2$) tetragonal phase has been found in both the VE-U8 corium and in samples from TMI-2 molten core. These results will be discussed with respect to the UO_2–ZrO_2 pseudo-binary diagram.

2. VULCANO VE-U8 spreading test: a severe accident experiment

2.1. VULCANO facility

At CEA-Cadarache, the PLINIUS European platform is devoted to R&D studies on severe accidents, using prototypic materials (i.e. using the UO_2 nuclear fuel, with depleted uranium) [7].

Within PLINIUS, the VULCANO facility [8] is composed of a furnace [9] and a test section, which is thoroughly instrumented. Post-test corium characterization is an important tool in the general understanding for the corium behaviour and for the possible solidification path [25]. For these reasons, this last point has been recently improved, especially X-ray diffraction (XRD), to obtain reliable data on the corium phases.

The VULCANO furnace uses the plasma arc transferred technology which allows complex oxide mixtures to be melted at high temperature ($T > 2000$ K). The mixtures to melt are inserted in the form of powders in a cylindrical rotating cavity (400 mm diameter–500 mm long). A self-crucible of zirconia is created in the furnace by the centrifugation and the heating of the partially stabilized zirconia powder. The heating process is controlled by optical pyrometry and in-board thermocouples. When a sufficient quantity of corium has been melted, the arc power is reduced and the cathode is withdrawn. The furnace is then tilted so that the melt pours out in the test section. In the VULCANO-E configuration, which is mainly devoted to the study of corium spreading, the test section consists of a spreading plane.

2.2. VULCANO VE-U8 spreading experiment

The VULCANO VE-U8 spreading experiment [1] is part of the European ECOSTAR project [6]. This test was representative of the flow of an in-vessel type corium only made of UO_2 and ZrO_2 over a test section made of lime-silica concrete. This configuration is characteristic (of some scenarios) for several current PWRs. For this test, an ‘in-vessel corium’ (target composition: 80 wt% UO_2–20 wt%ZrO_2) has been spread at ~2700 °C over a 20 wt% lime–80 wt% silica concrete. For this test, special attention has been paid to post-test corium characterization, especially, the X-ray diffraction to identify the corium phases. Four samples representative of the spread corium have been analysed and have shown the same pattern.

3. X-ray diffraction analysis of corium phases

3.1. Main corium phases

The main crystalline phases of corium are $U_{1-x}Zr_xO_2$ solid solutions. Their crystallographic structure is fluorite-like, with Fm3m (cubic) or P42/nmc (tetragonal) space groups. Many studies [10–20] have tried to determine domain of stability in temperature and in composition between the two crystalline forms.

Using Dae-Jon Kim equations [21], we were able to calculate the Vegard's law reported as Eq. (1) for $U_{1-x}Zr_xO_2$ cubic solid solutions [22].

$$\text{Fm3m} \quad a = 5.468 - 0.3296x \tag{1}$$

where a is the cubic cell parameter in Å.

As the domain of tetragonal solid solutions stability is for $x > 0.7$ (at adequate temperature [19]), we have calculated Vegard's law for the cell parameters a and c of the tetragonal structure from accurate data on cell parameters in this domain [22]: pure tetragonal ZrO_2 extrapolated from ambient temperature and $U_{0.21}Zr_{0.79}O_2$ experimental measurement [17]. The results are reported in Eqs. (2) and (3). The Vegard's law (Eq. (2)) for the a parameter fits more closely to experimental points [15] than the equation given for the c parameter (Eq. (3)) [22]: there is a linear variation of the a experimental lattice parameter unlike the c experimental parameter from $x = 0$ to 0.7. So, the Vegard's law with a lattice parameter (Eq. (2)) has been chosen for the corium phase determination of the stoichiometry of the tetragonal solid solution $U_{1-x}Zr_xO_2$.

$$\text{P42/nmc} \quad a = 3.9065 - 0.3095x, \tag{2}$$

$$c = 5.5125 - 0.3095x \tag{3}$$

where a and c are the tetragonal cell parameters in Å.

It must be stressed that the P42/nmc crystallographic group has been taken as geometric cue to perform the calculation of the stoichiometry.

3.2. Phase analysis of corium using X-ray diffraction

Many specific difficulties may occur with XRD corium analysis, which can be overcome: a good angular accuracy is necessary to distinguish superimposed peaks, and a good signal/noise ratio to detect minor phases. After acquiring the diffraction pattern, the identification of the phases comes next. As there is no reliable standard file [23] for the $U_{1-x}Zr_xO_2$ solid solutions, cell parameter refinements have been calculated for each crystallographic structure, then the stoichiometries have been estimated using Vegard's law (Eqs. (1) and (2)). Note that we consider the influence of the O/M ratio on the cell parameters to be negligible compared to the influence of the U/Zr ratio; this has been verified using the Rietveld method on diffraction pattern of well characterized corium samples [22]. If we consider an over-stoichiometry in oxygen, the maximum variation of the lattice parameter is 3×10^{-2} Å. That means for a solid solution $U_{1-(x-\Delta x)}Zr_{x-\Delta x}O_{2+y}$, the maximum cation content variation will be $\Delta x = 9 \times 10^{-2}$ for the maximum value at $y = 0.25$.

For quantitative analysis, after experimental studies, the Rietveld method has been chosen. As UO_2 and ZrO_2 have very different linear absorption coefficient, 2800 cm^{-1} and 600 cm^{-1} respectively, contrast of absorption between extremes solid solution, as well as between the main phases and the minor ones, certainly occurs, leading to micro-absorption. To solve this problem, a particularly fine grain size distribution of the powders has to be achieved. When resorting to these precautions, it is therefore possible to apply a correction to the weighting by Brindley's factor. The Rietveld method without calibration has then given very accurate results with an accuracy of ±2%.

The measurements were obtained with a Siemens-Brücker D5000 diffractometer using a plane post-sample mono-chromator in graphite, and a special nuclear sample-holder in order to have a well-maintained reference plane. No other treatments other than single peak refinements for qualitative analysis and Rietveld refinements for quantitative analysis have been conducted, i.e. we do prefer to simulate Kα2 and background during the refinements rather than to subtract them by mathematical ways [22].

3.3. Application of the X-ray analysis to the VULCANO VE-U8 experiment and to TMI-2 severe accident

3.3.1. Main corium phases for VULCANO VE-U8 experiment

For the VULCANO VE-U8 corium samples [22], at first sight, the pattern (Fig. 1) can be described as an angular distribution of groups of peaks, distribution similar to a fluorite structure with lattice parameters between those of UO_2 and cubic ZrO_2. A closer look (Fig. 1, zoom) shows that each group of peaks is made of one to two major peaks surrounded by two weak peaks. The strong peaks have been indexed to a tetragonal structure P42/nmc (see Table 1), and the weak peaks to two cubic structures Fm3m. For these last two phases, X-ray pattern accuracy is not sufficient to distinguish between cubic and tetragonal structures. For the main peaks in each

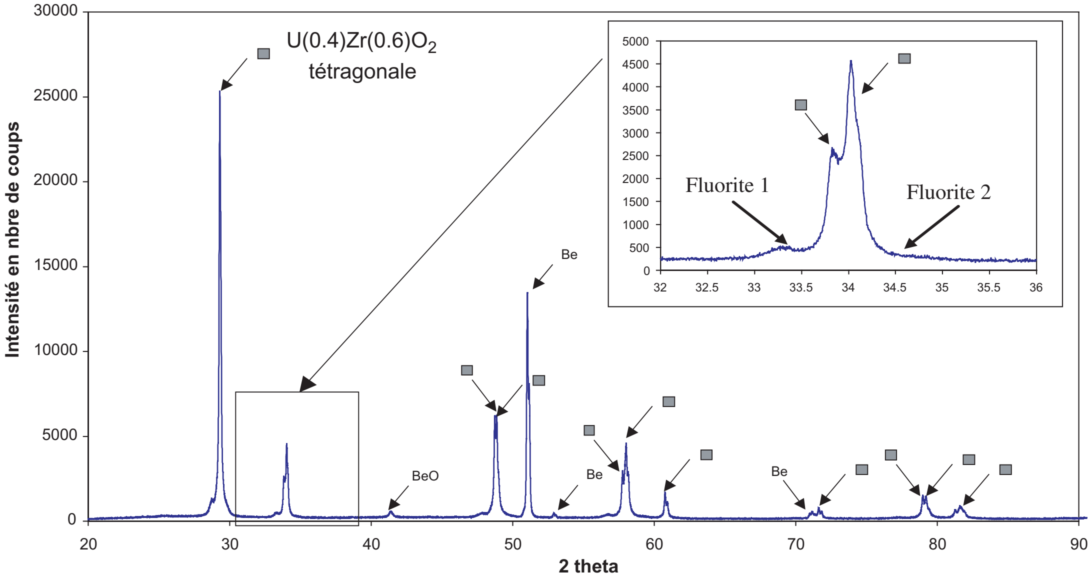

Fig. 1. Pattern of the VE-U8 sample.

Table 1
Peak indexation for the main corium phases (VULCANO VE-U8)

Miller indices	Measured intensities (%)	Theoretical intensities for tetragonal ZrO_2 (%)
101	100	100
002	10	8
110	17	13
112	32	33
200	17	17
103	13	11
211	26	21
202	9	5

group, single peaks were detected only at $2\theta = 29°$ and $61°$ (first and sixth groups of peaks respectively). Therefore, this is a clear evidence of the tetragonal structure.

Using unit cell refinement with the crystallographic structures found for the three phases, the cell parameters have been estimated (see Table 2) with the corresponding merit coefficient (R) for the three corium. Then, thanks to the previously determined Vegard's law (Eq. (2)), the phase stoichiometry has been calculated for the tetragonal phase. Note that for the fluorite 2, the merit coefficient (R) is bad: its value reaches 23%, due to low intensities and high peak superposition with the main phase. Nevertheless, for the main corium phase (tetragonal phase), the stoichiometry calculated with Eq. (2) shows a good merit coefficient ($R = 1.9\%$).

In conclusion, it has been shown that the main corium phase of VULCANO VE-U8 experiment is a tetragonal solid solution: $U_{0.4}Zr_{0.6}O_2$, with respect to the P42/nmc space group. This result is confirmed by Rietveld refinement of a specific pattern of the sample; this method gives a weight percentage of 90% for the main phase.

3.3.2. Main corium phases of TMI-2 NPP severe accident

The TMI-2 nuclear severe accident happened in March 1979. A mechanical failure in a pressure relieve valve produced a loss of coolant so that it eventually caused the heating and melting of the nuclear core. Different R&D programs have been conducted, especially the corium coming from the damaged core has been carefully analysed [24]. Four distinct regions have been distinguished to identify the damaged core: a cavity, a bed of loose debris, a consolidated, previously molten, ceramic material enclosed in a metallic crust and supporting fuel rod stubs and peripheral fuel assemblies. Some samples have been analysed on a diffraction patterns Guinier–Hagg camera. Thirty-four diffraction patterns have been conducted on TMI-2 corium samples from the ceramic melt, the lower plenum, and the lower crust [24].

Four solid solution families have been identified in the TMI-2 corium samples:

1. Cubic solid solutions (fluorite) up to 80% to 90% vol. in all samples.
2. Monoclinic solid solutions, interpreted as $U_{1-x}Zr_xO_2$ solid solutions, with $x = 0.9$.
3. Tetragonal solid solutions, attributed to $U_{1-x}Zr_xO_2$ solid solutions with $x = 0.75$.
4. Ferrite spinel (Fe, Ni, Cr, Al).

Special attention has been paid to the identification of the tetragonal phase (third family). For the estimation of the stoichiometries, we can see in Table 3 that stoi-

Table 2
Unit cell refinement and stoichiometries for the corium phases (VULCANO VE-U8 samples)

Phases	R (%)	Unit cell (Å)	Stoichiometries[a]
Fluorite 1	3.9	$a = 5.385 \pm 10^{-3}$	$U_{0.7}Zr_{0.3}O_2$
Tetragonal	1.9	$a = 3.725 \pm 10^{-3}$, $c = 5.298 \pm 10^{-3}$	$U_{0.4}Zr_{0.6}O_2$ (Eq. (2))
Fluorite 2	23.7[b]	$a = 5.21 \pm 10^{-2}$	$U_{0.2}Zr_{0.8}O_2$

[a] The x value is given with an uncertainty: 0.1.

[b] The R coefficient is bad due to very low experimental peak intensities and superimposition effect. Thus, the uncertainty on the lattice parameter increases of the Fluorite 2 the till 10^{-2}.

Table 3
Unit cell refinement and stoichiometries for the corium phases (TMI-2 samples)

		$U_{1-x}Zr_xO_2$ cubic (1)	$U_{1-x}Zr_xO_2$ cubic (2)	$U_{1-x}Zr_xO_2$ tetra
Lattice parameter (Å)	a	5.4596–5.4475	5.442 and 5.404	3.66
	c	–	–	5.26
x [24]		0.03–0.08	0.09 and 0.17	0.75
x Calculated by [22]		0.03–0.06	0.08 and 0.19	0.80

chiometries estimated by Brown et al. [24] match rather well with stoichiometries calculated with the proposed Vegard's law (Eq. (2)) [22]. The tetragonal phase has been found mainly in the lower plenum of TMI-2 reactor (10 wt%) [24]. This result shows that the formation of the $U_{1-x}Zr_xO_2$ solid solution tetragonal phase is not a VULCANO test effect and can exist according to specific conditions (cooling, range of compositions) in case of severe accident in a nuclear plant.

4. Discussion

The UO_2–ZrO_2 phase diagram which is usually taken as reference is shown in Fig. 2 [3]. The experimental points [10–12,14–16] and the modelling [3,5] of this phase diagram are in good agreement. It can be noted the solubility limit of the uranium in ZrO_2 for the tetragonal phase has no clear experimental evidence (see Fig. 2). Nevertheless, recent experimental results have shown that the solubility limit in the $U_{1-x}Zr_xO_2$ tetragonal phase is $x = 0.8 \pm 0.05$ at 2025 °C [18].

For the VULCANO VE-U8 experiment, there is 90 wt% of a tetragonal P42/nmc solid solution with the following composition $U_{0.4}Zr_{0.6}O_2$. It must be stressed that this solid solution composition does not exist in the reference phase diagram UO_2–ZrO_2 at thermodynamic equilibrium.

For TMI-2 severe accident, there is up to 10 wt% in the lower plenum debris part of a tetragonal P42/nmc solid solution with the following composition $U_{0.25}Zr_{0.75}O_2$. Again, this tetragonal composition does not exist at the thermodynamic equilibrium.

Nevertheless, such tetragonal solid solution compositions had been already observed by Cohen and Schaner in 1963 [15]. The two phases region (face centred cubic + face centred tetragonal) exists from 1660 °C up to 2300 °C in the ZrO_2 rich region. The appearance/disappearance of the tetragonal solid solution in the range of high uranium content (depleted in zirconium: $x < 0.5$) is directly linked with the formation of meta-stable phases. The formation of the meta-stable tetragonal phases can be attributed to the following mechanism: the diffusion-less transformation similar to the one observed in martensitic phase transformation, explained by kinetics and micro-structural factors. This transformation is responsible of the destabilization of the cubic into a tetragonal phase for composition $x > 0.4$. From $x = 0.5$, the phase is tetragonal with an acicular structure of the crystallites indicating that the phase transformation occurred on cooling (diffusion-less transformation below 2100 °C). From these experimental data, a

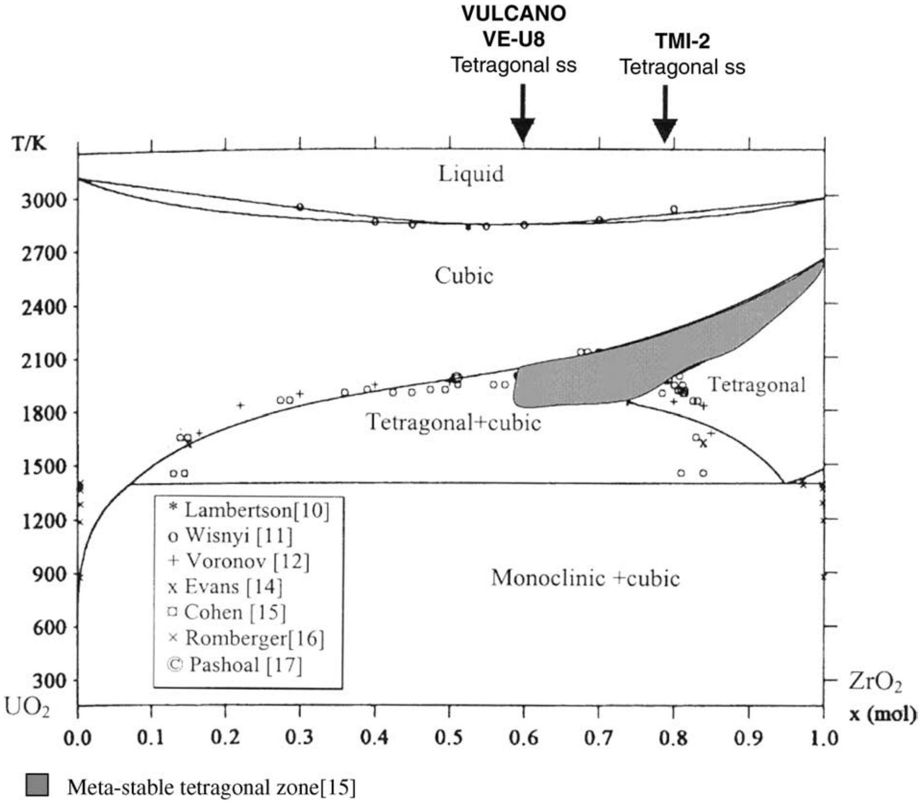

Fig. 2. UO_2–ZrO_2 phase diagram [3,22] and VULCANO VE-U8 and TMI-2 corium compositions.

meta-stable phase diagram has been proposed including the tetragonal meta-stable region [15]. VULCANO VE-U8 and TMI-2 corium samples can be represented in this meta-stable region (see Fig. 2).

For severe accident analysis, these results have strong consequences because non-thermodynamic-equilibrium modelling is not currently available, which means that thermophysical properties cannot be reliably estimated. On the other hand, the appearance of such meta-stable phases can give interesting information on the cooling rate of the corium. So, during TMI-2 severe accident, in some areas of the lower plenum, like for the VULCANO VE-U8 experiment, the thermal equilibrium has not been reached and the corium underwent a high cooling rate or it is the result of specific inner constraints during the cooling, loading to a special micro-structure.

5. Conclusion

In the framework of the severe accident R&D studies led by CEA, an in-vessel corium (UO_2–ZrO_2 mixture) spreading experiment (VULCANO VE-U8) has been performed. Post-test characterization techniques of such materials have been recently improved, especially with the X-ray diffraction (XRD) techniques to identify the corium phases. Corium phases are mainly $U_{1-x}Zr_xO_2$ solid solutions, but up to now, very few or no data were existing for the $U_{1-x}Zr_xO_2$ tetragonal solid solutions. Thanks to this work that developed XRD analysis, it is now possible to identify very precisely the corium phases, especially the solid solutions, and also to quantify them [22].

Zirconium-rich tetragonal $U_{1-x}Zr_xO_2$ solid solutions have clearly been identified in corium from VULCANO VE-U8 experiment as have been already noted by Brown et al. [24] in TMI-2 corium samples. However an extended range of compositions with high uranium content up to 40 mol% has been observed in the VULCANO VE-U8 corium whereas the maximum content for TMI-2 corium samples was 20 mol%.

This tetragonal solid solution is not marked in the equilibrium UO_2–ZrO_2 phase diagram [3,22] and was proposed by Brown as a meta-stable phase for Zr contents of 80 mol% and more [24]. We have proposed an extended range for the meta-stable tetragonal solid solution down 60 mol% in the phase diagram.

The solid solution probably occurs through a diffusion-less transformation as in pure zirconia. Unfortunately such meta-stable phases are not taken into account in modelling, despite notable consequences for its thermophysical properties (for example thermal conductivity and hence coolability). Furthermore, the appearance of meta-stable phases gives important information on the corium's cooling rate and so on the course of the accident.

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