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AN INTERPRETATION OF THE OBSERVATIONS PERFORMED ON RASPLAV AW200-1 CORIUM

Département d'Etudes des Matériaux
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RESUME:

The RASPLAV test AW-200-1, performed in the Kurchatov Institute in 1996, showed unexpected results: elevated measured temperatures and stratification of the C-22 corium. Thermalhydraulic and thermodynamic calculations allowed us to give some explanation of the phenomenon which took place in the device: due to the large range between the solidus and the liquidus temperature of the initial mixture, and due to the density difference between the liquid and the solid phase in this temperature domain separation of these two phases had happened during the melting of the mixture (we have no explaination why this separation occured). GEMINI2 calculations of the solidification paths are consistent with metallographic analyses which were carried out in these two separated layers after solidification.

MOTS CLES: corium, severe accident, Rasplav, thermodynamic
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Introduction

The RASPLAV AW200-1 test was performed in Kurchatov Institute in 1996, and showed unexpected results:

- elevated temperatures were measured in the pool, with a difference of 180 K between the centre (2950K) and the lateral upper part (2770 K) of the melt,
- stratification of two layers has been observed after the opening of the facility (see annex).

This paper is presenting a coupled thermal-hydraulic and thermodynamic explanation of these experimental observations and of the metallographic measurements which have been made on the solidified corium after the test.

Description of the AW 200 - n°1 test

The test principle can be rapidly described with the following sketch. The heat is produced by coupling high frequency heating on graphite walls, and the "cylindrical" walls are water cooled. The corium is separated from the graphite by means of Ta and W sheets.

The inner surface of the "cylindrical" walls are protected with C-100 briquettes (100 % oxidic corium), whose thermal conductivity is low in order to increase the molten inner part.

The composition of the inner corium is C-22, in which 22 weight percent of the total zirconium is oxidised, with the following molar composition:

- 58,3 mol % O
- 25,6 mol % U
- 16,1 mol % Zr

During the melting, the maximum measured temperature was about 2950 K in the middle part of the pool, which is higher than the liquidus temperature of the initial mixture (T liquidus of C-22 is about 2735 K).

The measured temperature in the lateral upper part of the melt is 180 K below the previous one, i.e. 2770 K. This difference cannot be explained by a superheating of the pool because of the relative small heat fluxes (~0.1MW/m²) and low viscosities. Thermal-hydraulic calculations estimate that the temperature difference inside the pool could not exceed 10 K.
Another result is observed on a sketch of the device after the test (see annex), that shows clearly the stratification of two layers in the melted zone. Metallographic analyses have been done: it was found that these two layers (among which one is more metallic (light) and the other more oxydic (grey)), are also themselves composed of two phases, being also for one of them more metallic (light phase) and the other more oxidic (grey phase), in different proportions. In the following part of this document, the measured composition of each layer and of each constitutive phase will be compared to the results of equilibrium calculations, obtained with the GEMINI2 software and its associated corium data base.

**Experimental results**

The experimental results are given in the form of volumetric fractions. In order to compare them to the Gemini2 results, they have to be transformed into mass or molar fractions. In order to get the mass fractions, we used the densities which were given in the RASPLAV paper [1] for the light and the grey phases:

\[
\rho_{\text{grey}} = 9750 \text{ Kg/m}^3 \\
\rho_{\text{light}} = 7500 \text{ Kg/m}^3
\]

If we estimate the top layer and main corium density by a classical mixture law

\[
\frac{1}{\rho} = \sum x_i \rho_i
\]

in which \(x_i\) and \(\rho_i\) are respectively the weight fraction and the density of the "elementary species" (here the grey and light phase), we find the following values:

\[
\rho_{\text{top layer}} = 8050 \text{ Kg/m}^3 \\
\rho_{\text{main corium}} = 9200 \text{ Kg/m}^3
\]

The experimental results are summarised in the following table:

<table>
<thead>
<tr>
<th>Atomic composition</th>
<th>Grey phase</th>
<th>Light phase</th>
<th>Grey phase</th>
<th>Light phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOP LAYER (20 vol% ~ 18 w%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grey phase</td>
<td>29.6 vol.%</td>
<td>35.3 w.%</td>
<td>75 vol.%</td>
<td>79.6 w.%</td>
</tr>
<tr>
<td>Light phase</td>
<td>70.4 vol.%</td>
<td>64.7 w.%</td>
<td>25 vol.%</td>
<td>20.4 w.%</td>
</tr>
<tr>
<td>U</td>
<td>30.7</td>
<td>1.4</td>
<td>29.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Zr</td>
<td>5.3</td>
<td>79.2</td>
<td>8.1</td>
<td>56.8</td>
</tr>
<tr>
<td>C</td>
<td>0.1</td>
<td>6.2</td>
<td>0.2</td>
<td>36.3</td>
</tr>
<tr>
<td>O</td>
<td>63.9</td>
<td>13.2</td>
<td>61.8</td>
<td>5.4</td>
</tr>
<tr>
<td>MAIN CORIUM (80 vol% ~ 82 w%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Thermodynamic calculations and discussion**

The first idea to explain the stratification of the corium is that the average composition may be located in the miscibility gap of the ternary system U Zr O that exists at elevated temperatures above 2770K (see figure 1).
**FIGURE 1**: Ternary section in the U O Zr system according to equilibrium calculations (GEMINI2 - TDBCR971) at 2873 K (from THERMODATA/INPG/CNRS)

Composition of C-22:
- 25.6 mol % U
- 16.1 mol % Zr
- 58.3 mol % O

(noted O on the diagram)
Thus, the separation could occur at temperature above 2770K, and during solidification, the two layers would remain separated. But this hypothesis does not fit the experimental scenario for the following reasons:

- The location of the average composition in the ternary system U O Zr can be seen on figure 1. This point is out of or very close to the limit of the miscibility gap, depending on the modelling of the miscibility data that is assumed. In any case, even inside the miscibility gap, the mass or volumetric fraction of the two phases that might separate would be about 1 or 2 % of "metallic" liquid for 99 or 98 % of oxidic liquid, and would not fit the experimental observations (about 20 vol.% of "metallic" phase went up in the RASPLAV device).

- The density of the "metallic" liquid in the case of non-miscibility was estimated about 20 % heavier than the "oxidic" liquid according to calculations made by DCC/SPEA [2]. It would thus separate downwards and not to the upper part of the pool.

- This phenomenon of liquid phase separation wouldn't explain the elevated temperature measured in the main part of the corium.

Therefore, we assumed another scenario of separation, supposed to happen during the melting of the corium. The figure 2 shows the phases which are in equilibrium versus temperature for a C-22 corium according to GEMINI2 calculations.

![Figure 2: phases in equilibrium for a C-22 corium](image)

From these curves it can be observed that a "metallic" liquid (mainly composed of \( \alpha \text{Zr}(O) \)) co-exists with the oxidic solid \((\text{U},\text{Zr})\text{O}_2\) over a large temperature range (from 2200 to 2700K at least).

It is possible to imagine that the liquid may gather through the microstructure, just before the liquidus temperature of the mixture is reached.

At the same time, because of its lower density (the liquid contains mainly Zr and O as the solid is constituted of \(\text{UO}_2\)), the liquid is supposed to separate, and go to the upper part of the pool. The reason for this separation is not understood.

The liquidus temperature of the solid phase, isolated from the liquid one which has separated, may thus reach the liquidus temperature of the residual oxide \((\text{U},\text{Zr})\text{O}_2\) about 2970 K, which would then
be the boundary temperature for the lower pool thermalhydraulics according to reference [3]. This could explain the elevated measured temperature in the lower molten part.

Assuming this scenario, it is then possible to calculate the equilibrium state after solidification, considering each phase separated from the other.

For the calculations, two parameters are not fixed:

1) the temperature at which the separation is supposed to occur,
2) the fraction of metallic liquid left in the main corium.

The effect of different hypotheses concerning these two parameters are discussed below. The reference parameters we have considered are the following: the separation is supposed to occur at 2700K and 10 mol% of the metallic phase (existing at 2700K in the equilibrium described in figure 2) remains within the main corium. This situation is depicted on following figure:

These best parameters values are described by the following scheme:

90% of the liquid in equilibrium with the solid at T=2700K

TOP LAYER or
Layer A

Liquid within the solid phase

Remaining solid + 10% of the liquid at T=2700K

MAIN CORIUM or
Layer B

90% of the liquid is assumed to separate at 2700K, and 10% of this liquid thus remains in the solid phase.

We will see in the next paragraphs that this temperature choice fixes the composition of the liquid contained in the layer A. The composition of the layer B is also determined both by the temperature and by the quantity of remaining liquid in the main corium.

We calculated the solidification of the two parts (layer A and layer B) separately, applying a Gulliver-Scheil model (no back diffusion in the solid).

**Solidification of the top layer A**

Taking the composition of the liquid in equilibrium at 2700 K (hypothesised separation temperature) from the previous GEMINI2 calculation for C-22, a new equilibrium calculation is made for its solidification, decreasing the temperature from 2700K (this top layer is already liquid at 2700K) to 1500 K (below 1500K, no new phases appear): the results (see figure 3) have to be compared to the experimental analysis of the "top layer" (see table 1).
The FCC-C1 quantity that solidifies from this liquid (40 mol% at 1500K or 27 w%) depends on the temperature assumed for the separation of the two layers.

If we assume a separation of the liquid from the solid at a temperature lower than 2700K, the relative proportions of solidified FCC_C1 and metallic phases would have been different (lower % for FCC_C1 (about 15 mol% at 2300K) and higher % for the other phases).

The next table gathers experimental values and calculated ones: they are discussed later.

<table>
<thead>
<tr>
<th>TOP LAYER</th>
<th>RASPLAV test</th>
<th>GEMINI2 results</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass %</td>
<td>grey phase</td>
<td>35,3</td>
</tr>
<tr>
<td></td>
<td>light phase</td>
<td>64,7</td>
</tr>
<tr>
<td>Grey phase (oxydic phase)</td>
<td>% at. U</td>
<td>30,7</td>
</tr>
<tr>
<td></td>
<td>% at. Zr</td>
<td>5,3</td>
</tr>
<tr>
<td></td>
<td>% at. C</td>
<td>0,1</td>
</tr>
<tr>
<td></td>
<td>% at. O</td>
<td>63,9</td>
</tr>
<tr>
<td>Light phase (metallic phase)</td>
<td>% at. U</td>
<td>1,4 (1.5)*</td>
</tr>
<tr>
<td></td>
<td>% at. Zr</td>
<td>79,2 (84.4)*</td>
</tr>
<tr>
<td></td>
<td>% at. C</td>
<td>6,2 (0)*</td>
</tr>
<tr>
<td></td>
<td>% at. O</td>
<td>13,2 (14)*</td>
</tr>
<tr>
<td>Ratio U/Zr (mol)</td>
<td>0,36</td>
<td>0,36</td>
</tr>
<tr>
<td>mass %</td>
<td>U</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>46,3</td>
</tr>
</tbody>
</table>

*: these values are deduced from the Rasplav report assuming no carbon is present, to compare to GEMINI2 results, which don't take into account the C.

**TABLE 1**: comparison of experimental and calculated results about compositions in the top layer (Layer A).
**Solidification of the main corium (layer B: solid + 10% of C-22 equilibrium liquid at 2700 K)**

The initial composition of this layer is given by the same calculations at 2700K (figure 2), taking the composition of the solid phase (FCC_C1) and 10 mol % of the liquid phase existing at this temperature for C-22.

As the molar ratio between FCC_C1 and liquid at 2700K was 70/30 in the global equilibrium previously calculated (figure 2), the new ratio of light phase in this mixture (solid + 10% of liquid at 2700 K) is

\[
\frac{10\% \times 30\%}{10\% \times 30\% + 70\%} \approx \frac{3}{73} \approx 4\%
\]

This main corium (layer B) is thus composed at 2700K of 4 mol% of light phase and 96 mol% of grey phase.

Applying once more a Gulliver-Scheil model for solidification, between a higher temperature than previously (the liquidus temperature is about 2970 K) and 1500K, the result (see figure 4) is a very elevated percentage of oxidic solid. These results have to be compared to the experimental data measured on the "main corium" (see table 2).

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**Figure 4: solidification of the main corium (layer B)**

![Figure 4: solidification of the main corium (layer B)](image-url)
The elementary composition of the grey phase is very close to the calculations results for the top layer and for the main corium. The agreement is not so good for the light phase. It may probably be explained first by the quantity of carbon that was found in this phase: the carbon comes from impurities in the original briquettes of C-22, and may also come through the atmosphere in the Rasplav device. This carbon may stabilise zirconium in the form of ZrC, and thus may enrich this light phase in Zr more than calculated by GEMINI2, which doesn't model ZrC.

Another point in favour of this explanation is the dispersion of the analyses results obtained in this phase (the values of the tables 1 and 2 are average ones): some of the experimental results may concern quasi-pure ZrC, and other U-rich parts of this phase.

The next point that may be noticed is the disagreement of the calculated mass ratio between the light and the grey phases compared to the measured ones (it was not the case in the previous table for the top layer).

The first idea, to overcome this problem, is to increase the quantity of "liquid that remains within the solid phase at the separation temperature", in order to improve this ratio. This was done without great success: in order to fit the experimental ratio of 80/20 and because of the great density difference between the light and the grey phase, the liquid quantity remaining in the solid has to be taken very elevated. Such an elevated value leads to a modification of:

- the liquidus temperature of the layer B, which decreases considerably with light phase addition, which then would not fit the experimental measured temperature in the central part of the device and would not explain the difference of 180K between the center and the lateral part of the mixture,
- the volumes of "metallic" and "oxidic" layers, which then would no more agree with the volumes measured in the AW 200-1 test (20 vol.% of "metallic" phase went up in the RASPLAV device).
However other aspects should be considered, which are not taken into account in the present study:

- the temperature within the melt was certainly not homogeneous, thus the temperature at which separation may occur may depend on the location in the melt,
- the separation was not complete: more light phase has been found in the upper part of the main corium than in the lower part.

Another possibility is to increase the quantity of liquid remaining within the main corium and also to decrease the separation temperature.

In order to conclude about uncertainties, it is also important to notice that the volumetric fractions values which are given in the Rasplav reports seem not to be consistent: it was found 20 vol% of light phase inside the main corium and at the same time, 20 vol% of stratified top layer (mainly constituted of light phase). These figures seem elevated compared to the initial mass of C-22 zirconium (about 17 w%): one of these volumic fraction or both ones may be overestimated.

Finally, due to the relative good agreement of all the other results, and due to the mentioned remaining uncertainties, we did not try to improve our calculations further. Therefore, those points are to be studied more precisely in the interpretation of the future experiments (AW200-2, Tulpan...), to get a better understanding of the phenomena.

**Conclusion**

Thermalhydraulic estimations and thermodynamic calculations allowed us to propose an interpretation of the results of the RASPLAV AW200-1 test, in which a separation of the C-22 corium in two layers was observed.

The process we described and calculated in this paper led us to explain the elevated measured temperatures, the metallographic analyses results and the understanding of the physical phenomena that happened during the experiment.

The major uncertainties of this analysis is the temperature at which the separation of the two phases occurs during the melting, and the respective quantities that effectively separate.

The final question that is remaining is the following: "is this separation process during the corium melting a system effect in the RASPLAV device, or is it a generic effect that could be found in a reactor situation?"

Some analytical experiments have necessarily to be planned to answer this question.

**REFERENCES**

1 RASPLAV AW-200-1 : Post test examination of ingot, presented by Yu. Degaltzev to 6th Rasplav PRG Meeting, 18-20 mars, 1997, Moscow, Russia
2 Internal information
3 J.M. SEILER, Nuclear Engineering and Design, 166 (1996) 259-267
"Phase segregation model and molten pool thermal-hydraulics during molten core-concrete interaction"
Longitudinal section scheme of ingot RASPLAV AW-200-1

1. Loading height before experiment
2. Loading height after experiment
3. C-22 briquettes
4. Cavities
5. Top layer
6. Main corium melt