Philipp Pöml* and Boris Burakov

Study of the redistribution of U, Zr, Nb, Tc, Mo, Ru, Fe, Cr, and Ni between oxide and metallic phases in the matrix of a multiphase Chernobyl hot-particle extracted from a soil sample of the Western Plume

https://doi.org/10.1515/ract-2018-2957
Received March 15, 2018; accepted June 27, 2018; published online July 20, 2018

Abstract: A “hot particle” found 6 km west of the Chernobyl nuclear power plant 4 years after the Chernobyl severe nuclear accident was analysed by scanning electron microscopy and electron probe micro-analysis. The matrix of the particle consists of relics of partly molten UO₂ nuclear fuel and two different phases of solidified U–Zr–O melt (U₀.₇₇Zr₀.₂₃O₂ and U₀.₆₇Zr₀.₃₃O₂). The particle also contains a unique metallic inclusion of a size of 30 × 22 μm. The inclusion is non-homogeneous and in some parts shows a dendrite-like structure. It consists of about 38 wt.% Fe, about 10 wt.% U, Mo, and Nb, about 5 wt.% Ru, Zr, Ni, and Cr, and small amounts of Tc (2 wt.%) and Si (0.4 wt.%). The presence of partly molten nuclear fuel suggests a local temperature exceeding 2850 °C. The metallic inclusion most likely formed when steel, fuel, and cladding reacted together and molten steel incorporated U, Zr, Nb, Tc, Mo, and Ru from molten fuel and cladding during a very fast high-temperature process. Fast quenching of the metallic and the oxide melt left no time for Tc and Mo to evaporate. Molten Zr was partly oxidised and acted as a buffer for O which caused the reduction of a fraction of the U. The data of this study support the previously reported supercritical nature of the Chernobyl explosion.

Keywords: Severe nuclear accident, Chernobyl, EPMA, hot particle.

1 Introduction

The Chernobyl nuclear accident happened on 26 April 1986 (USSR, now Ukraine) and was accompanied with the release of highly radioactive solid particles (ranging in size from less than 1 μm to hundreds of μm). These so-called “hot particles” are the subject of intensive investigation since immediately after the accident until present time [1–25]. This is mainly for two reasons: (1) the necessity to evaluate the long-term ecological consequences of contaminated soil; and (2) to understand the physico-chemical interactions which took place during the Chernobyl nuclear accident progression for input to severe nuclear accident models and to improve nuclear power plants (NPP) design safety features.

Chernobyl hot particles have been found in Ukraine [2, 9, 11, 12, 15, 18–20], Belorussia [2, 10], Sweden [1, 4], Hungary [5], Poland [3, 7, 8, 16], Germany [16], and many other countries such as Norway, Lithuania, Finland, Greece, Bulgaria, Austria, Czech Republic [14].

Surprisingly, the phase and chemical compositions of Chernobyl hot particles are not simply made-up of fragments of mechanically destroyed RBMK-1000 U-oxide fuel and Zr-cladding. A significant amount of hot-particles extracted from soil samples of the Western Plume in the 30 km exclusion zone around the Chernobyl NPP consist of various solid solutions of UO₂–ZrO₂ [12, 15, 17, 20, 22]. Some hot-particles are enriched in ¹⁰⁶Ru, some samples also have ⁶⁰Co, ¹²⁵Sb, and contain the metallic phase Fe–Cr–Ni [18, 20]. Round-shaped hot-particles found in Sweden [1] and Ukraine [19], were reported as pure metallic Ru. Metallic particles consisting of alloys of Fe–Ni–Mo–Ru–Tc–Pd–Rh were identified in Poland and Germany [2, 16].

One unique metallic hot particle from a soil sample collected from under the Western Plume at a distance of 6 km from the Chernobyl NPP in 1990 consists of an inhomogeneous Zr–U alloy (with some tiny veins enriched mainly in U and Nb) [12, 17]. A recent study of this latter particle concluded that the process of interaction between nuclear fuel and cladding during the accident lasted only for some microseconds or less [25].

The origin of oxidised hot particles that are solid solutions of UO₂–ZrO₂ can be explained by high-temperature (≥2600 °C) interaction (melting) between the UO₂ fuel matrix and Zr-cladding that happened in a local part of the reactor core before the explosion [12, 15, 17, 20].
The formation of the metallic hot particles is not so clear. The irradiated UO₂ fuel matrix contains metallic inclusions (so called “white inclusions”) of Mo–Ru–Tc–Pd–Rh alloys [26]. The size of these round inclusions is burn-up dependent. For UO₂ fuel the size of the white inclusions was described as not exceeding 5 μm [27] whereas for U–Pu oxide fuel they are typically 5–10 μm and rarely exceed 20 μm [28]. Mechanical destruction of the fuel may cause release of these inclusions in the form of individual particles, however, the composition of Chernobyl hot particles containing metallic matrices have been found to differ from the composition of white inclusions. The presence of some non-radioactive elements in these particle matrices means that they do not originate from the fuel. For example, the only source of Nb is the cladding (Zr + 1 wt.% Nb) or RBMK pressure tubes (Zr + 2.5 wt.% Nb) [29]. Stainless steel of the fuel rod spacing grid is the most realistic source of Fe, Cr, and Ni [29]. At least part of the molybdenum in metallic hot particles could originate from the fuel fission products, the alloy of the spring (Zr + 0.7 wt.% Mo + 0.7 wt.% Cu) used in every fuel pin (Figure 1), or the stainless steel used for the fuel pin spacing grid that can contain up to 0.5 wt.% Mo [30, 31].

It can be concluded from the existing data on metallic hot particles that a high-temperature interaction of steel, cladding and UO₂ fuel including the elements of the white inclusions took place. However, it remains unexplained why elements such as Mo and Tc were not oxidised and/or evaporated during such a high-temperature process.

In this paper we present a detailed analysis of a unique multiphase hot particle extracted from a soil sample of the Western Plume (6 km from Chernobyl NPP) in 1990 that shows the redistribution of U, Zr, Nb, Tc, Mo, Ru, Fe, Cr and Ni between oxide and metallic phases. The study of this particle could explain and predict some important physico-chemical features of the high-temperature interaction between U-oxide fuel, Zr-cladding, and stainless steel, which may happen during a severe accident in different types of nuclear reactors.

Table 1: Conditions used for quantitative electron microprobe analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>X-ray line</th>
<th>Diffracting crystal</th>
<th>E₀ (kV)</th>
<th>I₀ (nA)</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>Kα1</td>
<td>Quartz 101̅1</td>
<td>15</td>
<td>20</td>
<td>U</td>
</tr>
<tr>
<td>Zr</td>
<td>Lα1</td>
<td>PET</td>
<td>15</td>
<td>20</td>
<td>Zr</td>
</tr>
<tr>
<td>Fe</td>
<td>Kα1</td>
<td>Lithium flouride</td>
<td>15</td>
<td>20</td>
<td>Fe</td>
</tr>
<tr>
<td>Nb</td>
<td>Lα1</td>
<td>PET</td>
<td>15</td>
<td>20</td>
<td>Nb</td>
</tr>
<tr>
<td>Cr</td>
<td>Kα1</td>
<td>Quartz 101̅1</td>
<td>15</td>
<td>20</td>
<td>Cr</td>
</tr>
<tr>
<td>Ni</td>
<td>Kα1</td>
<td>Lithium flouride</td>
<td>15</td>
<td>20</td>
<td>Ni</td>
</tr>
<tr>
<td>Mo</td>
<td>Lα1</td>
<td>PET</td>
<td>15</td>
<td>20</td>
<td>Mo</td>
</tr>
<tr>
<td>Tc</td>
<td>Lα1</td>
<td>Quartz 101̅1</td>
<td>15</td>
<td>20</td>
<td>Virtual</td>
</tr>
<tr>
<td>Ru</td>
<td>Lα1</td>
<td>PET</td>
<td>15</td>
<td>20</td>
<td>Ru</td>
</tr>
<tr>
<td>Si</td>
<td>Kα1</td>
<td>TAP</td>
<td>15</td>
<td>20</td>
<td>Si</td>
</tr>
</tbody>
</table>

*PET, Pentaerythritol.
*TAP, Thallium acid phthalalate.

2 Methods

The Chernobyl “hot” particle #S1 investigated in this study was mounted in acrylic resin and ground/polished manually using diamond paste to a flat surface. Electron probe microanalysis (EPMA) for the elements U, Zr, Fe, Nb, Cr, Ni, Mo, Tc, Ru, and Si was carried out using a shielded Cameca SX100R. The analytical conditions are given in Table 1. The acceleration voltage was 15 kV at 20 nA beam current. For Tc no reference material was available. Instead, the intensities of Mo Lα and Ru Lα were measured and linearly interpolated for the intensity of Tc Lα as a virtual reference material. For data acquisition the Probe for EPMA software [www.probesoftware.com] and for matrix correction the full PAP procedure [32] was used.

The analysis points of the particle’s matrix were carefully chosen according to the phases’ BSE contrast. For quantification the results were classified into three phases: (1) Zr below 0.5 wt.%, (2) Zr below 10.5 wt.%, (3) Zr above 10.5 wt.%.

3 Results

Figure 2 shows a backscatter electron (BSE) image of the polished surface of hot particle #S1. The particle is about 190 × 130 μm in size. From the BSE contrast and quantitative X-ray maps of U and Zr (Figure 3) three different phases can be distinguished in the particle matrix, shown as dark, light grey, and white contrasts in the BSE images. The chemical compositions of the three phases
The metallic inclusion has a size of 30×22 μm. Figure 4 shows a BSE image and quantitative X-ray maps for U, Zr, Fe, Nb, Cr, Ni, Mo, Tc, Ru, and Si of the inclusion. The inclusion is non homogeneous and in some parts shows a dendrite-like structure. It consists of about 38 wt.% Fe, about 10 wt.% U, Mo, and Nb, about 5 wt.% Ru, Zr, Ni, and Cr, and small amounts of Tc (2 wt.%) and Si (0.4 wt.%). Table 2 shows the average chemical composition of the inclusion. From the X-ray maps three main phases can be identified: (1) A phase containing the metals Fe, Zr, Mo, Tc, Cr, Nb, and Si, (2) a phase containing Ru, Ni, and U, and (3) a phase with relatively high Fe content.

### 4 Discussion

The morphology of the large patches of almost pure UO₂ in the particle matrix (Figure 2, bright BSE contrast) suggests that they are most likely residual, partly molten UO₂ fuel. The small amount of Zr found in this material is either related to a diffusion process or, more likely, Zr produced by fission. The measured Zr amount (0.12 wt.%) fits to the expected Zr produced by thermal neutrons in ²³⁵U-based nuclear fuel at about 13 MWd/

---

**Figure 2:** BSE image of the multiphase hot particle #S1 extracted from a soil sample of the Western Plume (6 km from Chernobyl NPP). The white arrow marks the metallic inclusion. In the oxide matrix three different phases can be distinguished according to their BSE contrast (dark, light grey, white). The phases are UO₂–ZrO₂ solid solutions of different compositions (see Table 1).

**Figure 3:** BSE electron image and quantitative X-ray maps of U and Zr showing the three different UO₂–ZrO₂ solid solution phases in the matrix of hot particle #S1.

**Table 2:** Quantitative EPMA data in wt.% for the main phases in the hot particle #S1.

<table>
<thead>
<tr>
<th>Phase</th>
<th>BSE contrast</th>
<th>U</th>
<th>Zr</th>
<th>O</th>
<th>Total</th>
<th>N*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Dark</td>
<td>71.61</td>
<td>13.53</td>
<td>14.37</td>
<td>99.51</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Light grey</td>
<td>76.90</td>
<td>8.59</td>
<td>13.35</td>
<td>98.83</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>White</td>
<td>85.35</td>
<td>0.12</td>
<td>11.52</td>
<td>96.98</td>
<td>18</td>
</tr>
<tr>
<td>Metallic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inclusion</td>
<td>U</td>
<td>11.92</td>
<td>5.49</td>
<td>37.82</td>
<td>50.23</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td></td>
<td>5.49</td>
<td>37.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td></td>
<td></td>
<td>8.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nb</td>
<td></td>
<td></td>
<td>3.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td></td>
<td></td>
<td>5.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td></td>
<td></td>
<td>9.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td></td>
<td></td>
<td>2.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tc</td>
<td></td>
<td></td>
<td>6.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td></td>
<td></td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td></td>
<td></td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*N, Number of analyses.
kgU burn-up (average burn-up at the time of the accident [33]). The presence of the patches of almost pure UO₂ fuel and their morphology also indicates that at least part of the fuel was molten. This points to a local temperature exceeding 2850 °C. The structure of the matrix of the particle suggests that at some point partly molten fuel was surrounded by a liquid melt. The melt then started to solidify, first a phase with higher Zr content forming smaller patches (light grey) followed by the solidification of the remaining melt (with the highest Zr content) along the boundaries of the already solid material (dark). This sequence of solidification respects the UO₂–ZrO₂ phase diagram keeping in mind that the process was quick and in a non-equilibrium state [34].

A sample with a structure similar to this particle was reproduced experimentally under vacuum at 2600 °C with a melting time of 15–20 s [12]. The experiment involved melting a piece of non-irradiated RBMK UO₂ fuel in contact with a piece of RBMK Zr-cladding. However, under these conditions no almost pure UO₂ relics were found, which could be explained by a slower heating rate and more time for the fuel to react when compared to the Chernobyl conditions.

The discovery of a large metallic inclusion (30 × 22 μm) in a rather large hot particle (190 × 130 μm) with an oxide UO₂–ZrO₂ matrix is unique. Previously described hot particles were either individual metallic or oxide particles or aggregates of discrete particles. Most likely the metallic inclusion has formed by the interaction of fuel, cladding, and fuel pin spacing grid steel inside a pressure tube. Fe, Cr, and Ni originate from the stainless steel, which is most likely also the source of Si, because the RBMK-1000 spacing grid steel could contain up to 0.8 wt.% Si [30, 31]. The Zr-cladding (Zr + 1 wt.% Nb) is a likely source for Zr and Nb. Tc, Ru, and Mo could originate from the white inclusions in irradiated nuclear fuel. Mo, however, could also originate from the steel of the spring inside a fuel pin (Figure 1) or the spacing grid steel. Note, however, that the steel of the spring also contains 0.7 wt.% Cu and no Cu could be detected in the metallic inclusion or the hot particle matrix.

In a previous study a number of smaller (4–14 μm) metallic hot particles of similar composition to the presented metallic inclusion were analysed by qualitative and quantitative EPMA [3]. Those particles were collected in 1986 in northern Poland. The detected elements were Fe, Ni, Mo, Tc, Ru, Rh, Pd, and U in different proportions, however, the presence of Cr, Zr, and Nb was not reported. The authors concluded their particles represented white inclusions of irradiated fuel that were mechanically

![Figure 4: BSE image and quantitative X-ray maps of the metallic inclusion in hot particle #51.](image-url)
ejected from the destroyed reactor core of the Chernobyl NPP. The authors based their conclusion on the observations that (1) their hot particles contained similar elements and (2) were of similar size to the white inclusions. They assumed that the Fe and Ni they observed also originated from white inclusions. This was never reported in the studies that described metallic precipitates in irradiated nuclear fuel [27, 28, 26]. In addition, the size of metallic precipitates in irradiated UO₂ fuel with a burn-up of around 46 MWd/kgU are reported to be up to 5 μm [27]. Since the average burn-up of the fuel in the 4th unit of the Chernobyl NPP was about 13 MWd/kgU at the time of the accident [33] white inclusions of a size smaller than 5 μm can be expected in the fuel. This is significantly smaller than the metallic hot particles described in [3].

In the present study, the chemical composition of the metallic inclusion suggests that it was formed as a result of the interaction of molten spacing grid steel, cladding, and nuclear fuel at very high temperature. During this process the molten steel extracted and incorporated other metals from molten fuel and cladding. In particular the presence of Tc and Ru in the metallic inclusion, whose only source are the white inclusions in the irradiated fuel, can only be explained by melting of the fuel (at least 2850 °C).

Normally volatile elements like Tc and Mo were not oxidised and evaporated but remained in metallic form. The presence of metallic U even suggests that part of the U was reduced. The most reasonable explanation for such a behaviour is a very fast high-temperature process previously suggested [12, 15, 20, 25]. Such a process would have occurred in a local part of the reactor core before the explosion, followed by very fast quenching of the melt during/after the explosion, leaving no time for the oxidation of elements like Tc and Mo. Molten Zr was partly oxidised during the reaction with the molten fuel, acting as a buffer for O. This supported the reduction of a fraction of the U up to metallic state and hence the partitioning of U and Zr into the melt forming the metallic inclusion.

5 Conclusions

The results obtained from the study of a multiphase Chernobyl hot particle allows us to make the following conclusions:

1. The high-temperature process (at least 2850 °C) in a local part of Chernobyl NPP 4th unit reactor core before the explosion involved not only nuclear fuel and Zr-cladding but also stainless steel of fuel pin spacing grids. During this process the molten steel extracted and incorporated U, Zr, Nb, Tc, Mo, and Ru from molten fuel and cladding.
2. Very fast quenching of immiscible metallic Fe–Cr–Ni–U–Zr–Nb–Tc–Mo–Ru and oxide Zr–U–O melts during/after the explosion, left no time for the oxidation and evaporation of Tc and Mo – at least from the metallic melt.
3. Molten Zr from the cladding was partly oxidised during the reaction with the molten fuel, acting as a buffer for O and forming a non-homogeneous and non-stoichiometric (with the lack of oxygen) Zr–U–O melt. This caused the reduction of a fraction of the U up to metallic state that explains the presence of U in the metallic inclusion.
4. The observations described above show no evidence for the occurrence of a steam-zirconium reaction as a cause for the Chernobyl explosion. The previously suggested hypothesis of the supercritical nature of the Chernobyl explosion [25, 35–37] is supported by the current study.
5. The new information obtained in this study on a unique Chernobyl hot particle supports the development of new computer codes for severe nuclear accident modelling of different types of nuclear reactors.

Acknowledgement: The authors greatly acknowledge financial support from IAEA in the framework of the Coordinated Research Project on Management of Severely Damaged Spent Fuel and Corium. The sample was provided by the V.G. Khlopin Radium Institute within the collaboration agreement between JRC Karlsruhe and KRI.

References