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Application for beam time at ESRF – Experimental Method

Proposal Summary (should state the aims and scientific basis of the proposal) :

The main objective of this project is to investigate the local structure of corium like materials that result from the melting of a nuclear reactor core. Prototypical corium materials are synthesised at the JRC-ITU by Sol-gel methods and fully characterised using analysis methods such as XRD, RAMAN, IR, NMR etc. Laser heating experiments will also be performed, where samples are heated and cooled at controlled atmosphere simulating high temperature phase changes during severe accidents. In addition, samples with Pu content typical of corium formed from a melted MOX fuel will be prepared and analysed in a similar manner. This will include samples doped with 1% 238Pu to investigate self-irradiation damage.

In order to fully understand the behaviour of such materials, oxidation state, geometric and electronic structure data must also be determined. X-ray methods available at ESRF will provide key elements for understanding the local electronic structure (determined by EXAFS) and the chemical state (from XANES).

This work is part of the post-doctoral project of Emtethal Kassim.

Scientific background :

In the last forty years there have been at least three major nuclear accidents with damage to reactor core; one with low and two with massive release of radioactivity to the atmosphere (Three Mile Island, Fukushima and Chernobyl, respectively). In all cases the fuel melted, reacted with the cladding and progressed in a molten form to varying extents within the reactor building and beyond. The reaction products formed are commonly termed "Corium", which is initially composed of ZrO_2 and UO_2 and is formed by reaction between the molten fuel and the Zircaloy cladding, which oxidises to form the ZrO_2. Other constituents in the Corium develop according to its interaction with the structural materials of the reactor, with steel and concrete being major contributors, should the molten fuel progress significantly. The Corium will also contain significant contents of Pu due to in-situ breeding processes and/or use of MOX fuel as was the case at Fukushima Daiichi.

Many studies have been made on corium in the past [1-4], but have largely concentrated on its behaviour when melted in the core, and in the main have been large scale prototypical engineering tests to understand the phenomena that could occur during such accidents. These investigations proposed here form part of a major project to investigate the properties of corium itself in the cooled state, starting with its most simple composition $(U,Zr)O_2$ at different molar ratio and being extended systematically to include structural materials such as Cr, Fe and Ni (from steel) and Al, Mg and Si (from concrete). Macroscopic properties such as thermal conductivity, melting temperature, hardness (essential for core remediation and recovery) will be determined. Understanding of these properties is of potential interest in order to support decommissioning and enclosure strategies but also to assess the state of the corium with respect to long term structural stability and to provide input to safety analysis.

These studies will be underpinned by detailed modelling of the materials and their resistance to irradiation damage and potential corrosion from the surroundings. Such advanced modelling based on ab initio calculations and molecular dynamics can only be achieved if a substantial body of geometric and electronic structure data are available. In particular, the local electronic structure (determined by EXAFS), unoccupied density of states and chemical state (from XANES) are key elements in the development of models for these systems, and can be used in qualification of the simulations themselves. These X-ray methods available at ESRF will be coupled to other structural methods (XRD and 17O and 91Zr MAS-NMR) to provide the greatest possible understanding of the materials at the nanometer and atomic scale.

Dedicated $(U,Zr)O_2$ samples across the full stoichiometry range will be prepared and those with similar composition to existent corium will be doped with 239Pu and 238Pu as a means to investigate the damage caused by self-irradiation of these materials, a phenomenon that will occur in reality, as although no more fission occurs, radioactive decay of fission products and actinides will continue during the time required to remove the fuel from the damaged core.

Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity...etc) :

The samples will be prepared at the JRC-ITU using sol gel methods, which given the full mixing of the actinide ions in solution will provide material with very similar structure to that obtained during a molten reaction in a reactor core, which in the main cools slowly (due to a low conductivity of the oxide crust) under thermodynamic equilibrium conditions. Along with the end members ZrO2 and UO2, samples with 20, 40, 50, 60, and 80 mol% mixtures will be prepared to establish this information for the full system. Under certain circumstances (rapid interaction with massive volumes of water) Corium cools rapidly yielding a single cubic phase; to examine this material samples from the FARO tests (quenching of hundreds of kilos of corium in water) are also available. Furthermore, under a controlled atmosphere, prototypical corium samples at different molar concentration will be melted using laser heating method implied at ITU. The molten crust will then be analysed in order to determine phase changes occurring at high temperatures during accidents.

Corium has a Zr content of about 40 mol%. At this composition a further sample will be prepared with Pu content typical of a corium formed from a melted MOX fuel. Finally, a sample doped with 1% 238Pu will be prepared to investigate self-irradiation damage in the material. XAS acquisition will be performed on a total of 15 (+ 2 ex FARO) samples, including the UO2, PuO2 and ZrO2 references. The proposed materials are listed in Table 1.

The samples will comply with radioprotection requirements at the ESRF beamline (mass, limit activity, isotopic composition, etc.).

For each sample and depending on the probed atom, K, LII and LIII edges will be collected in both transmission and fluorescence modes. Based on our previous XAS experiments on ROBL beamline [5-11], 2 hours of data collection are needed per U and Zr edge, while more time is needed for the low Pu content (in total 94 h measuring time for all samples and references (see table 1). Therefore, a total of 12 shifts (4 days) are required for this project.

Beamline(s) and beam time requested with justification :

For each sample and depending on the probed atom, K, LII and LIII edges will be collected in both transmission and fluorescence modes. It is estimated that approximately 6 hours are needed per sample and 2 to 4 hours per reference material. Therefore, a total of 12 shifts on the ROBL beam line are required for this experiment. The additional time corresponds to cooling down and warming up cycles, sample set-up, handling in the glove box and energy changes.

Results expected and their significance in the respective field of research :

This work will contribute towards understanding the local structure of corium materials.

Thorough studies and detailed modelling of the material will be carried out in order to understand the local structure of lavas formed in nuclear reactor accidents.

With the help of other analysis performed at ITU, XAS data will provide precious experimental information for a final assessment of the U-Zr-O and U-Pu-Zr-O phase diagram at high temperature.

A standard activity report will be issued at latest 2 months after the end of the project. Furthermore, scientific publications will be written and submitted at the end of the project and both TALISMAN and ESRF will be acknowledged

References

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