1. Background and objectives

- Investigation of characteristic data of fuel debris for its removal operation and appropriate management
- Factors affecting debris characteristics specific to the Fukushima accident
  - Seawater injection, no reflood: salt deposit on high temp. corium
  - BfC control blade: chemical form of boron in solidified core melt?
  - MOX fuel, FPs
  - Large amount of MCCl products at the bottom of containment vessel
- Lab-scale experiments on simulated debris to understand the above factors

2. High temperature reaction between (U,Zr)O₂ and sea salt deposit

- Simulated corium: (U₃₋₂Zr₂O₇)O₂ (metastable fcc), (U₁₋₂Zr₂O₇)O₂ (tet.+mon.)
- Salt powder prepared from natural seawater:
  - NaCl : MgO: 6H₂O : MgSO₄ : H₂O / CaSO₄ / KCl = 87.9/5.8/2.9/1.8/1.7 (mol%)
- Isothermal treatment and analyses (XRD and SEM/EDX)
  - Powder mixture / corium pellet in salt bed
  - 815 ~ 1395 °C, 2 ~ 20 h, under Ar or air flow
  - Thermal decomposition of salt components
  - Vaporization of NaCl above Mp. (800 °C+)
  - Stable, crystalline MgO from chloride and sulphate
  - CaO (?) from sulphate, most reactive with corium
  - Evolution of HCl (corrosive) and SOX (oxidizing) gases
- Reaction products depends on oxygen partial pressure (pO₂)
  - Under high pO₂ where UO₂ is stable:
    - Dense Ca+(Na⁺)-U-O uranate layer on the corium surface
    - (U,Zr)O₂ oxidized to orthorhombic U(V)-Zr-O and U₂O₂-ZrO₂ ss.
  - Under low pO₂, where U₂O₅ is stable:
    - (U,Zr)CaO₂ partial solution on the corium surface
    - But low diffusivity of CaO

3. Characterization of solidified core melt involving BfC control blade

3.1. Phase identification in arc-melted specimens

- Investigating the phase relationships in the solidified core melt (ex. molten pool)
- Fuel materials: (U,Zr)O₂, Zr
- Control Blade materials: BfC, SS316L
- Arc melting of compacted mixtures under Ar atmosphere, subsequent annealing under Ar or Ar-0.1%O₂ atmosphere
- Phase identification on the cross section by XRD and SEM/EDX

Example of the arc-melted mixture of BfC/SS/Zr(U,Zr)O₂ reaction product. The pellet surface is covered by the typical orange-coloured uranate layer. (Air atmosphere, 1002 °C, 12 h)

(Left) Cross sectional SEM image of sea salt(U₃₋₂Zr₂O₇)O₂ reaction product. The pellet surface is covered by the typical orange-coloured uranate layer. (Air atmosphere, 1002 °C, 12 h)

(Right) Stable reaction products shown on the UO₂-U₂O₅-U₂O₇ boundary diagram.

3.2. High temp. oxidation behaviour

- Annealing of a piece at 1500 °C for 10 h under pO₂=1×10³ atm (=steam cond.)
- Metallic part remelted during the isothermal treatment
- Zr and U in the alloy, Zr in ZrB₂, selectively oxidized : (Zr,U)O₂ scale formed on the surface, instead the (Fe,Cr,Ni)B matrix extensively formed inside
- No ferrous oxides formed under this condition

3.3. Microhardness of phases in solidified core melt

- A basic mechanical property for considering machining tools for debris removal
- Employed a micro Vickers tester
- Borides, especially ZrB₂, are considerably harder than any other materials: potentially barrier for cutting tools

Schematic of the phase relationships in the solidified BWR core melt as a function of the initial BfC/Zr ratio, under low oxygen partial pressures.

4. Other research works ongoing

- Phase relationships in U-Zr-O system under oxidizing condition (U₂O₅ domain)
- Phase relationships in simulated MCCl product : arc melting (homogeneous melt) or light-concentrating heating (temp. gradient) of concrete/SS/Zr(U, Zr)O₂ system
- Bulk mechanical properties for machining tools: compressive strength, Young's modulus, fracture toughness, etc.
- Chemical behaviour of debris in water (boric acid, hydrogen peroxide, etc.)
- Development of debris dissolution technique for destructive chemical analysis
- Effective use of TMi-2 debris specimens for verification

5. Conclusions and Acknowledgements

- Various types of simulated fuel debris specific to the Fukushima accident were prepared and characterized to contribute for the removal operation and management
- Among the sea salt components, CaO decomposed from sulphate was found to be most reactive with (U₂O₅) corium. The reaction products depends on the oxygen partial pressure, in other words, the oxidation state of uranium.
- The phase relationships in the BWR-type core melt were investigated. ZrB₂ and ferrous borides potentially form in the alloy matrix of Fe-Cr-Ni and (Fe,Cr,Ni)B(Zr,U). These borides are extremely hard materials.

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References