Characterization of U / Nd microspheres synthesized by internal gelation

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Motivation

In the context of advanced nuclear fuel cycles including partitioning and transmutation, actinide co-conversion processes play an important role. Therefore, actinide ceramics are considered to be used as precursor for the fabrication of innovative fuels. A suitable conversion method is the sol-gel route by internal gelation [1,2]. It’s advantage is the prevention of dust formation during synthesis and the fact, that spherical particles are already formed at the gel stage. Within the project ASGARD preparation of UO2/Nd2O3 microspheres is studied.

Synthesis

1. Sol preparation

- Chemicals used:
  - ADUN
  - Nd(NO3)3 - 6 H2O
  - Urea
  - Hexamethylentetramine (HMTA)

- Acid deficient uranyl nitrate (ADUN):
  - Dissolution of UO2 in a saturated UO2(NO3)2 - 6 H2O solution [3,4].
  - UO2 prepared by thermal denititation of UO2(NO3)2 - 6 H2O [3].

2. Gelation [5]

- Decomplexation
  - UO2(NO3)2 + 2 CO(NH2)2 ⇌ [UO2]2+ + 2[NH2]2+ + 2 NO3-
  - HMTA protonation & decomposition
    - (CH2)6N4+ + 2 H+ ⇌ (CH2)3N+ + H3+ + 6 CH2O

- Hydrolysis
  - UO2(NO3)2 + 2 H2O ⇌ UO2(OH)2 + 2 H+ + NO3-
  - UO2(OH)2 + 2 H2O + Nd(NO3)3 

Gelation temperature: 90 °C

3. Washing & aging

- Petroleum ether (2x)
- Aging in NH4OH at RT
- Washing with NH4OH (2x)

4. Drying at air (RT)

5. Thermal treatment

- 1300 °C for 2h (3 °C/min)
- H2:Ar (4:96), 1.2 L/min

Characterization

Preparation of particle compositions with Nd contents in a range of 0 – 40 %.
- ICP-MS analyses of dissolved particles in HNO3 to calculate χ(Nd)ICP-MS:
  - mole fraction: χ(Nd) = [Nd]/([U] + [Nd])
  - Mass and diameter distribution (optical microscopy).
  - SEM/EDX investigations.
  - X-ray powder diffraction analyses.

Results

- Pure uranium particles and microspheres containing Nd were prepared. Nd contents determined by ICP-MS:
  - 5.80 %, 11.99 %, 17.40 %, 22.62 %, 27.59 %, 33.49 %, 37.68 %, 42.63 %
- Average masses of 30 particles in a range of 4.8 - 5.6 mg were measured.
- Spherical shape was proven by optical microscopy, avg. diameters with small standard deviations were achieved.
- SEM observations confirm the spherical geometry, superficial cracks were found for the dried particles. Thermal treatment in H2:Ar led to microspheres with a proper surface integrity.

- Crack formation was additionally proven by ESEM, reducing the pressure from 850 Pa to 70 Pa.
- EDX results only represents the top 5 µm of the sample, they are in good correlation with the bulk values measured by ICP-MS.
- XRD plots show typical reflexes of a cubic phase, a small shift of the reflex position to higher 2θ values with increasing Nd content was found up to χ(Nd)ICP-MS = 22.62 %.
- The lattice parameter a depend linear on χ(Nd) for contents ≤ 27.59 %, particles with more Nd have a constant lattice parameter of a = 5.4595 Å.

Conclusion

- Spherical oxidic UNd particles with Nd contents in a range of 0 - 42.63 % were synthesized via the sol-gel method by internal gelation.
- Although the process was manual, average particle masses and diameters with small standard deviations were achieved.
- One cubic phase was observed for the treated microspheres for all investigated UNd compositions.

- However, the expected linear behavior of lattice parameter a according to Vegard’s rule was observed for compositions up to 27.59 % Nd, only.
- A higher sintering temperature and duration may lead to phases behaving linear for all prepared compositions.
- Single phase solid solutions of the sensitive UO2 / Nd2O3 system can be prepared by internal gelation with Nd contents up to 43 %.